Engaging communities to reduce toxic exposures with a field kit for mapping soil lead in Peru and New York

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ABSTRACT

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Lead is a global health hazard and reducing environmental exposures to lead is becoming increasingly important as negative health impacts are documented at lower levels of exposure. Soils, an important source of lead exposure in children, represent a largely untested reservoir of accumulated past and present lead contamination retained in the surface. Concentrations of soil lead are very spatially heterogeneous, however, and testing is required to identify whether site-specific soils present a hazard. In this dissertation I outline the several ways to increase testing and awareness about soil-lead contamination to provide individuals with the information needed to prevent exposure to soil lead. Chapter one presents a new field procedure for use by the general public to screen soils for hazardous levels of lead that is based on determining bioaccessible lead. Chapter two describes the delineation of soil-lead hotspots in four mining-impacted towns in Peru and reveals that parents using the field procedure identified a hotspot missed by previous testing. In this study, we find child blood lead information is associated with parent cleanliness, which may represent a pathway for child exposure to dust and soil lead, although no associations are seen directly with soil lead concentrations. In chapter three, Peruvian high school students use the field procedure in their science classes to identify hotspots of soil lead and share this information with their community. Finally, chapter four highlights that extremely elevated concentrations of soil lead are not limited to far-off mining communities but are also present locally in New York City. Soil core data collected does not reveal a single source or blanket atmospheric inputs, but rather highlights the variability of deposition that requires widespread testing.

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Part I

Introduction

Anthropogenic use of the toxic metal lead (Pb) has drastically increased Pb concentrations in the environment. Ice cores show elevated atmospheric Pb concentrations over the past two thousand years with rapid increases since the industrial revolution; Pb concentrations in ice cores also document historical events such as elevated levels during the Roman Empire [1] and extremely low levels during the black plague [2]. Although the toxic health effects of Pb are well established, its widespread past and present use in batteries, paint pigments, cable coverings, radiation shielding, bullets, plumbing, solder, and gasoline is because of several useful properties such as a malleability, anti-corrosive nature, density, and low boiling point [3].

0.1 Health impacts of Pb

Lead (Pb) is highly toxic to all organ systems, but its harmful effects on the nervous, renal, and cardiovascular systems are the best characterized [3–9]. At extremely high blood lead levels (BLL) >100 μg/dL, Pb can lead to abdominal pain, cerebral edema, encephalopathy, seizures, and death [3,7,9]; records indicate the acute effects of high doses of Pb were known in Roman times [10, 11]. At high BLLs (>40 μg/dL), Pb is linked to anemia, reduced fine and gross motor skills, reduced kidney function, vision and auditory impairment, increased blood pressure, and heart disease [7]. The U.S. Centers for Disease Control and Prevention (CDC) guidance recommends medical intervention at BLL > 45 μg/dL through chelation therapy [12]. At lower BLL levels, such as those more commonly seen in the U.S. today (<10 μg/dL) Pb is linked to decreased IQ, learning difficulties, [5, 6], cardiovascular disease [13], among others [3, 7, 14]. No studies have found a threshold values or minimal risk level for Pb [7, 9].

Children are at greatest risk of Pb poisoning because of their neurological development phase, their mouthing behaviors, and because their bodies absorb Pb at a higher rate [9]. Since no safe BLL has been identified, the U.S. CDC uses a reference level of the 97.5th percentile of children tested in the National Health and Nutritional Examination Study

(NHANES) to identify children with elevated BLL. In 2012, the U.S. CDC set the BLL reference level at 5 μg/dL, based on the 2010 NHANES study; this level should be updated to 3.5 μg/dL based on the 2015 NHANES data [12,14,15]. While BLLs in the U.S. have dropped precipitously from 99.8% (1976-1980) [16] of BLLs > 5 μg/dL to 0.5% (2013-2014) [15] of children tested, exposure to Pb remains a major public health problem in many low- and middle- income countries (LMICs) [4, 17].

0.2 Burden of disease

Lead contributes to 24.4 million disability-adjusted life years (DALYs) and 1 million deaths globally each year, 82% of which are in LMICs [17, 18]. These estimates underestimate the global burden of disease, however, because information on exposure to soil pollution is largely unknown [17]. Devastating cases of fatal Pb poisoning, while rare, still happen today. In artisanal gold mining communities in Northwestern Nigeria where families processed ore in the home, BLLs in 97% of 204 children tested > 45 μg/dL, and 82% of 118 children that passed away in the previous year had clinical symptoms of acute Pb poisoning. Chelation therapy, removal of contaminated soil, and preventing ore processing in living areas brought mortality rates down from 43% to < 1% [19]. In Kabwe, Zambia, BLLs in 50% of children living near an old mining complex tested > 45 μg/dL, and median soil Pb was often above 1000 mg/kg Pb and up to 3000 mg/kg Pb. Despite these elevated levels first reported in a 2003 to 2006 study, these conditions remained in 2014 [20, 21].

However, the majority of Pb poisoning, and those captured in global health assessments, continues at chronic exposure not leading to death. In Mexico, Pb is associated with 820,000 DALYs in children 0-4, and geometric mean BLLs are 8.9 μg/dL in urban areas and 22.2 μg/dL in rural areas [22]. At toxic waste sites in India, Indonesia, and the Philippines, Pb accounts for 63% of DALYs and a greater burden of disease than malaria [23]. Calculations of the economic cost of cognitive impairment due to Pb poisoning are staggering: each annual cohort of children born after Pb decreased in 1980 adds $110-300 billion in economic

productivity gains in the U.S. alone [24].

0.3 Exposure to Pb

The primary exposure routes for Pb are through inhalation and ingestion, though dermal exposure can be important for organic Pb compounds, such as tetraethyl Pb. Inorganic, soluble Pb < 2.5 μm in size is almost completely absorbed in the alveoli, and larger inhaled particles (> 2.5 μm) are incidentally ingested when they are cleared from the respiratory tract by the mucociliary escalator and swallowed [7]. Gastrointestinal absorption ranges from 3 to 26% in adults and 40-50% in children, and is dependent on whether ingested on a full or empty stomach, as well as age, nutritional status (e.g. iron deficiency and calcium intake), and the form of Pb ingested (e.g.mineralogy and particle size) [7, 25]. Absolute bioavailability (ABA) is generally defined as the fraction of ingested Pb that is absorbed in the gastrointestinal system and enters the bloodstream. Once in systemic circulation, Pb interferes with enzyme function through binding to sulfhydryl groups and impairs neuronal signaling by mimicking calcium [7, 10]).

Potential sources of environmental Pb include deteriorating Pb-based paint, water supply systems with Pb service lines or fixtures, and soil and dust contaminated from past and present Pb-emitting sources including Pb gasoline, deteriorating Pb-based paint, municipal waste incineration, smelters, mining, informal Pb-acid battery recyclers, and other industrial activities [3, 26]. The U.S. CDC also lists traditional folk medicine, makeup, candies from Mexico, accidental ingestion of toy jewelry, and cooking in traditional clay pots with Pb glazes as potential sources [27].

0.4 Lead exposure from soils

Important exposure pathways for children, who are most at risk of Pb poisoning, include incidental ingestion of contaminated soil, contaminated dust inside the home, and resuspended

Pb dust in air [28–31]. The fine soil fraction (<250 μm and <150 μm) in particular can stick to hands and toys, which young children often put in their mouths [26, 29, 32]. Several studies have demonstrated a clear correlation between soil-Pb concentrations and child BLLs [28–30, 33–35], and soil remediation has been linked to decreased Pb exposure [36]. Mielke and Reagan's review of studies with BLL and possible contributors of air, dust, soil, water, food, and paint demonstrated that 42 of the 46 studies with soil-Pb information found a positive correlation between BLL and soil-Pb [29].

Several health-based screening levels exist for soils though some lack enforcement power. New York State uses a Soil Clean-up Objective of 400 mg/kg Pb for restricted residential use [37], and California has a Human Health Screening Level of 80 mg/kg Pb estimated to raise child BLL by < 1 μg/dL [38]. The U.S. Environmental Protection Agency (EPA) continues to use a soil hazard standard from the year 1991 of 400 mg/kg Pb for bare soil where children play and 1200 mg/kg Pb for other residential soil [39]. Total soil Pb concentrations, and Pb bioaccessibility, is often spatially heterogeneous, a crucial fact that means once hotspots are identified they can be addressed and uncontaminated areas are likely nearby.

0.5 Community participation in testing

Soil Pb is often very heterogeneous and concentrated in hotspots, as has been documented by studies throughout the world [20, 40–42]. Although urban areas can exhibit a bulls-eye pattern of Pb concentrations [43], anthropogenic renovations and landscaping still result in specific homes, developments, and parks with low Pb levels located within a high Pb urban cores. This highlights the need for testing soil to identify contaminated areas, and community participation can be a valuable way to increase information about where hotspots are located. In addition, community participation in sampling, especially by parents or relatives of young children, may promote testing soil in the most crucial locations - where children live and play. Since many recommendations to address contaminated soil, such as covering contaminated soil with mulch or new soil and reducing the amount of soil brought into the home [44], rely

on the parent being aware of the contamination, involving residents directly in the sampling may be a good way to ensure that they are equipped with this knowledge and the key steps to prevent exposure to soil Pb.

0.6 Bioaccessibility

Since the absorption of Pb in the body depends on soluble Pb, properties of soil that release more Pb into solution such as particle size, mineralogy, and encapsulation can moderate the health impacts of Pb [7, 45]. Bioaccessibility methods use a simulated gastric solution to determine the amount of Pb released into solution [7, 46–48] and are thus more relevant to health hazard than measurements of total Pb concentration. These in vitro bioaccessibility (IVBA) methods estimate the relative bioavailability (RBA) of Pb in soil. Relative bioavailability (RBA) is the ratio of the absolute bioavailability (ABA), or fraction absorbed, of a soil sample to the ABA of a soluble form of Pb, such as Pb acetate. Based on studies in swine, the RBA of different minerals has been estimated, in decreasing order, as: cerrussite ($PbCO_3$), Mn(Pb) oxide, Pb oxide (PbO), Pb phosphate, Fe(Pb)oxide, anglesite ($PbSO_4$), galena (PbS) [7, 49].

0.7 Chapter overview

In chapter one, *A field procedure to screen soil for hazardous lead*, I describe the development of a new, simple field procedure designed for use by the general public to screen soil. The procedure is a modification of the *in vitro* bioaccessibility (IVBA) method from Drexler and Brattin [46] and EPA Method 1340 [50], and uses the same simulated gastric acid of a 0.4 M glycine solution at pH 1.5. Key modifications enable using this method in the field, notably a higher soil-to-solution ratio of 1:10 yielding the required higher Pb concentrations in solution that are needed to measure the extracts with a portable X-ray fluorescence (XRF) analyzer and to form a color precipitate with sodium rhodizonate. Soil samples can be classified based

on extractable-Pb concentrations as <200 mg/kg (low), 200-400 mg/kg (medium), and >400 mg/kg (high).

In chapter two, *Does involving parents in soil sampling identify causes of child exposure to lead? A case-study of community engagement in mining-impacted towns in Peru*, I describe a study in four mining-impacted communities in Peru to delineate soil Pb hotspots, identify possible sources of Pb exposure, and involve parents in screening soil with an earlier version of the field procedure. Roadside mapping by handheld XRF identified two hotspots of highly contaminated soil (1,000-6,000 mg/kg Pb); however, parent sampling found a third, previously missed, hotspot of Pb contamination. There was no clear relation between child blood-Pb levels and Pb levels in soil samples collected inside or outside the home. Instead, increased child blood Pb was associated with decreased level of cleanliness of parent clothing and shoes, linking a possible behavioral factor for transferring contaminated soil and dust to children. The findings highlight the feasibility and value of involving families in identifying environmental contamination and reducing exposure.

In chapter three, *Hazardous levels of lead in soil identified with a kit by students in high school science classes*, I discuss the results of integrating the field procedure into science classes in three Peruvian towns. Students learned about soil Pb hazards, how to prevent exposure, and then how to collect soil samples and analyze them for Pb. Follow-up XRF analysis of student samples confirmed high concentrations of soil Pb in Cerro de Pasco (2100±2000 mg/kg Pb) near an open pit mine, and in Callao (460±280 mg/kg Pb), near mineral ore storage facilities. Low concentrations were found in Ate (130±110 mg/kg Pb), about 0.5 km from a secondary Pb smelter. Students were able to collect data relevant to their families and their communities in class, and we suggest extending similar activities could be an effective way to generate the environmental data required to identify hotspots and teach students how to reduce exposure.

In chapter four, *Elevated lead (Pb) concentrations and inventories in New York City*, I share findings of elevated Pb concentrations in surface soils and in soil cores. I show first

that Pb concentrations in 370 surface soils from the backyards of 76 homes in Brooklyn and Manhattan far exceed the New York Soil Cleanup Objective and also exceed the Pb concentrations found in publicly accessible surface soils from 571 samples. Soil core inventories contain 71% and 51% of the expected ^{210}Pb and ^{137}Cs from atmospheric fallout, respectively, possibly due to disturbances in the soil profile and local variations in deposition. Total uncorrected soil Pb inventories are 290±220 g/m^2, which would increase drastically if corrected for ^{210}Pb or ^{137}Cs.

Part II

Main Chapters

Chapter 1

A Field Procedure to Screen Soil for Hazardous Lead

This chapter is published in Analytical Chemistry[1]

1.1 Abstract

Soils retain lead (Pb) contamination from possible sources such as mining, smelting, battery recycling, waste incineration, leaded gasoline, and crumbling paint. Such contamination is often concentrated in toxic hot spots that need to be identified locally. To address this need, a simple field procedure was designed to screen soil for hazardous Pb for use by the general public. The procedure is a modification of the *in vitro* soil-Pb extraction of Drexler and Brattin [46] and EPA Method 1340 and uses a 0.4 M glycine solution at pH 1.5. A higher soil-to-solution ratio of 1:10 allows for classifying soil samples based on extractable-Pb concentrations of <200 mg/kg (low), 200-400 mg/kg (medium), and >400 mg/kg (high) using sodium rhodizonate as a color indicator. The 1:10 soil-to-solution ratio also makes it possible to measure Pb concentrations in the glycine extract solutions on a continuous scale

[1]Franziska C. Landes, Anna Paltseva, Jennifer M. Sobolewski, Zhongqi Cheng, Tyler K. Ellis, Brian J. Mailloux, Alexander van Geen, "A field procedure to screen soil for hazardous lead," *Analytical Chemistry*, (2019) vol. 91, pp. 8192-8198. Available at https://pubs.acs.org/doi/abs/10.1021/acs.analchem.9b00681

using a portable X-ray fluorescence analyzer. The procedure rather consistently extracts about one third of the Pb extracted by the standard method across a wide range of Pb concentrations. Manufacturing the kit in larger quantities could reduce the cost of the materials well below the current $5 per test.

1.2 Introduction

Lead (Pb) is known to be highly toxic to all organ systems and is especially harmful to cognitive development in children [3, 5, 8, 51]. Ingesting soil contaminated with Pb is an important pathway for child exposure [28–31], and soil remediation has been linked to decreased Pb exposure [52, 53]. Soils in industrial and urban areas have accumulated Pb from deteriorating Pb-based paint, atmospheric deposition from leaded gasoline and municipal waste incinerators, as well as past and present industrial activities such as mining, smelting, and battery recycling [4, 17, 53, 54].

Poisoning from environmental contamination with Pb often goes undetected and is unevenly distributed [4,55]: 82% of deaths from Pb poisoning occur in lower- and middle-income countries (LMICs) [17]. Lead poisoning accounts for 63% of the disability-adjusted life years (DALYs) of toxic waste sites in India, Indonesia, and the Philippines, and contributes to a greater burden of disease than malaria in these countries [23]. Globally, the disease burden from Pb exposure is estimated to have caused 13.9 million DALYs in 2012 and 0.5 to 0.7 million deaths [56]. The disease burden and loss of cognitive function due to Pb poisoning have serious economic implications: Pb poisoning in urban Peru is estimated to cost the country 0.5% of its GDP [57]. In the U.S., each annual cohort of children born after 1980 is estimated to add $110-300 billion in economic productivity gains due to an increase of 2–5 IQ points from reduced Pb exposure [24].

Several studies have demonstrated a clear correlation between soil-Pb concentrations and child blood lead levels (BLL) [28, 30, 33, 34, 58]. In some cases, Pb exposure has been

correlated with the degree of urbanization because soils retain past Pb contamination [53, 58, 59]. Children under age 6 are the most vulnerable to Pb poisoning because they are in a crucial neurological development phase; they are also at higher risk for Pb exposure because they often crawl on the ground and place dusty toys and hands into their mouth. Although U.S. child BLLs declined by more than 90% after Pb was no longer added to gasoline and paint, the U.S. Centers for Disease Control and Prevention (CDC) recognizes that "no safe Pb level has been identified." In 2012, the CDC replaced its BLL of concern of 10 μg/dL with a reference level of 5 μg/dL for children [12, 14]. Reflecting this change, some U.S. states have updated their soil reference level to as low as 80 mg/kg [38], but the federal soil hazard standards remain at 400 mg/kg for bare soil where children play and 1200 mg/kg for other residential soils [39].

The Pb in soil that is bioaccessible or bioavailable provides a better estimate of health hazard than the total Pb concentration [48]. *In vivo* bioavailability tests require complex animal trials whereas *in vitro* bioaccessibility (IVBA) tests are less expensive substitutes based on laboratory extractions that simulate gastric conditions. Bioaccessibility methods measure the amount of Pb released from the soil in the simulated gastric solution and determine a relative bioavailability (RBA) that reflects the chemical form and matrix of the soil Pb [46, 47, 49]. Absolute bioavailability (ABA) is generally defined as the fraction of ingested Pb that is absorbed in the gastrointestinal system and enters the bloodstream. Relative bioavailability (RBA) is the ratio of the ABA of a soil sample to the ABA of a soluble form of Pb such as lead acetate.

There is increased interest in developing alternative methods to ease the determination of bioaccessible Pb [60]. One challenge of the existing methods for measuring bioaccessible Pb in soil is the need for costly laboratory equipment to process soil samples and measure Pb concentrations in the soil extract. The high spatial variability of total and bioaccessible Pb in soils [41, 59, 61, 62] means that many measurements are needed. Many LMICs do not have the resources needed to identify soil Pb contamination with the same methods used by

high-income countries, nor do they conduct routine screening of Pb in blood. A rapid and affordable field procedure could therefore considerably reduce human exposure by identifying hot spots of Pb contamination to avoid or address.

To the best of our knowledge, there is no field procedure to test for Pb in soils reliably, and no test kit for Pb in soil has been approved by the U.S. Environmental Protection Agency (EPA) [40]. The commercially distributed 3M^{TM} LeadCheck^{TM} swabs can only be used to test paint, which has a much higher Pb content than even the most contaminated soils [63]. The field procedure for soil presented in this study is derived from the IVBA method of Drexler and Brattin (2007) [46] and EPA Method 1340 [50] but uses a higher soil-to-solution ratio. The modification allows the detection of elevated bioaccessible Pb concentrations with sodium rhodizonate, the same indicator used to detect Pb in gunshot residue [64–66]. The modified procedure also makes it possible to use a portable X-ray fluorescence analyzer to measure bioaccessible Pb concentrations in the liquid extracts on a continuous instead of a categorical scale. Importantly, these modifications and new detection methods enable the procedure to be used in the field.

1.3 Materials and methods

1.3.1 Soil samples

All 137 soil samples were collected in the field and passed through a kitchen sieve with a 1 mm mesh size. The samples represent a variety of contamination types and come from six different countries, including 65 urban soil samples from New York City and 31 rural soil samples from Peru. The New York samples were collected from residential backyards (n=42), urban farms (n=3), and publicly accessible parks and tree pits (n=20). The Peruvian soil samples were collected from small mining-impacted communities along the Carretera Central east of Lima (n=10), the city of Cerro de Pasco built around a gaping open-pit mine (n=11), and the infamous smelter town of La Oroya (n=10). Researchers from Pure Earth (formerly

Blacksmith Institute) contributed an additional 41 soil samples from the following locations: a secondary lead smelter in India (n=8), a large secondary lead smelter of lead-acid batteries in the Philippines (n=4), an electronics-waste site in Uruguay (n=12), and informal lead-acid battery recyclers in Indonesia (n=10) and the Philippines (n=7).

1.3.2 Instrumental measurements

Total Pb concentrations in soil were measured in the laboratory with a portable handheld X-ray fluorescence (XRF) analyzer (Innov-X Systems DELTA Premium) in a benchtop stand. Sieved soil samples in 20 mL scintillation vials were sealed with plastic wrap, inverted on the benchtop XRF stand, and analyzed using the instrument's standard soil mode for 20 seconds at each of the three incident-beam energies. Soil samples were analyzed three times, shaking the vial end over end between each analysis in an attempt to capture soil heterogeneity. Results from XRF analysis of metals in soils, especially Pb, has been found to highly correlate with laboratory acid digestions [67,68] and is approved for use by EPA Test Method 6200 [69].

Concentrations of Pb in the field-procedure extract solutions were also measured by XRF and confirmed in a subset by a high-resolution inductively coupled plasma mass spectrometer (ICP-MS) (Thermo Scientific Element II or Perkin Elmer DRCe). For XRF analysis, 10 mL of the field-procedure extract solution was analyzed similarly to the soil samples, by inverting the 20 mL vial sealed with plastic wrap on the benchtop stand and using the instrument's soil mode for 20 seconds at each incident-beam energy. For samples containing <10 mg/kg Pb in solution, the analysis time was tripled, which lowered the detection limit calculated by the instrument's software from 5 to 1.5 mg/kg Pb. Concentrations of Pb in the Drexler and Brattin (DB) extract solutions were measured exclusively by ICP-MS, because the dilution of 1 g soil in 100 mL solution results in concentrations below the XRF detection limit. The XRF's accuracy for soil Pb measurement was verified with U.S. National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) soils including SRM 2710 with 5,532 mg/kg Pb (mean 93±1% SD of the reference value, n=27), SRM 2710a with

5,520 mg/kg Pb (103±2% n=3), SRM 2711 with 1,162 mg/kg (98±5%, n = 86), and SRM 2711a with 1,400 mg/kg (104±2%, n=27). At much lower Pb concentrations, XRF readings were too high at 128±17% (n=67) of the reference value for SRM 2709 of 18.9 mg/kg Pb. Soil XRF Pb data were not adjusted for this bias at low concentrations. Data for field-procedure extract solutions measured by XRF were corrected by subtracting 3.5 mg/kg Pb based on the repeated measurements of a blank extract solution. For ICP-MS analysis, data were accepted when concentrations of Pb obtained for NIST reference materials 1640A (mean recovery 104±3%, n=8) and 1643F (99±4%, n=8) were within 10% of their published values. All ICP-MS method and vial blanks contained <1 μg/L Pb.

1.3.3 Field procedure

The field procedure for assessing bioaccessible Pb was developed by modifying various steps of the IVBA method described in Drexler and Brattin (2007) and used in EPA Standard Operating Procedure (SOP) 9200.2-86 and EPA method 1340 [46, 47, 50]. Soils are sieved in the field, if possible, and otherwise dried overnight until sieving is achievable. For this study, three level scoops of sieved soil (0.5 mL each, approximately 1.5 g total) are weighed and added to 15 mL of a 0.4 M glycine solution adjusted to pH 1.5 with hydrochloric acid in a polyethylene scintillation vial with a Polyseal cone cap (Figures 1.1 and A.1). While weighing is not required for a field deployment, not doing so can add additional variability. The vial is agitated for 30 seconds at the beginning of the extraction to ensure that no sediment adheres to the bottom, and again after 45 minutes to promote mixing. To achieve a total extraction time of 1 hour and to allow soil particles to settle, the vial sits for an additional 15 minutes. Next, about 10 mL of the supernatant is filtered through a 0.45 μm disposable syringe filter into a clear vial using a syringe that fits within the opening of the vial. A 1-cm plastic spacer is placed on top of the vial to ensure that the tip of the syringe remains in the supernatant and does not take up soil that could clog the filter (Figure A.2). In a subset of analyses, different amounts of soil were extracted while maintaining the same

soil-to-solution ratio (0.5 g in 5 mL for 12 samples in 2014 and 1 g in 10 mL for 50 samples in 2015).

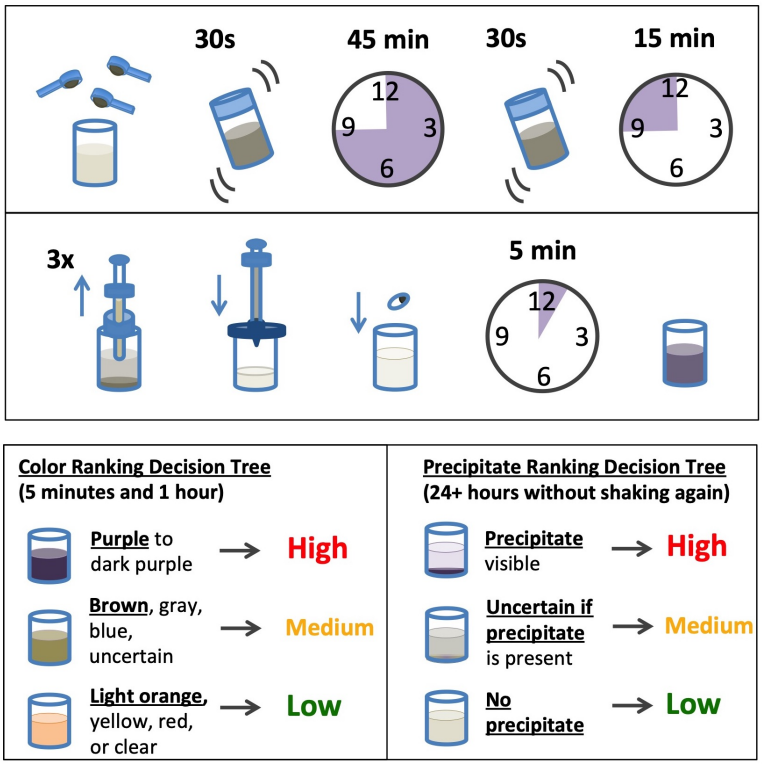

Figure 1.1: A schematic of the field procedure steps and a decision tree for the color ranking. A more detailed visual instruction sheet as given to those using the procedure in pilot studies can be found in Supporting Information (Figure A.2).

1.3.4 Color indicator

After filtering the extract, a dissolvable gelatin capsule containing 10 mg of sodium rhodizonate is added. Sodium rhodizonate forms a purple precipitate with Pb, as described by Feigl and Suter [64], and is still used today in forensic applications to identify lead gunshot residue [65, 66]. The intensity of the violet-purple color for each sample was ranked by two researchers independently as low, medium, or high after 5 minutes, based on the color chart (Figure 1.1). All vials had tape over the labels and were randomly ordered to ensure an unbiased reading.

All samples that were clearly purple were ranked high, and all samples that were orange,

yellow, clear, or red were ranked low. Samples that were brown, gray, blue, or appeared darker but not purple were ranked medium. In addition, one researcher ranked the color after 1 hr, based on photos that were taken during the procedure. One researcher also ranked the actual vials after 24 hr based on the amount of precipitate that was visible on the bottom of the vial. Samples were ranked highest if the precipitate covered the vial bottom and ranked high if any precipitate was visible. If no precipitate was visible, the sample was ranked low. Samples were ranked medium if the precipitate was barely visible, often appearing like a wisp of smoke in the solution.

1.3.5 Standard bioaccessible Pb method

For comparison, bioaccessible Pb was determined in a subset of 50 soil samples and 2 NIST soil standards following the standard method of Drexler and Brattin (DB) and EPA Method 1340 by extracting 1 g of dried soil <250 μm in 100 mL of 0.4 M glycine adjusted to pH 1.5 at 37°C for 1 hour [46, 50]. We used an incubator with a shaker table at 37°C and 30 rpm, instead of the prescribed end-over-end rotator in a water bath; samples were turned end over end every 10 minutes by hand to simulate the end-over-end rotator. The pH was measured at the end of the extraction to confirm that it remained within 0.5 units of 1.5. The Drexler and Brattin method establishes IVBA and can be used to estimate RBA by calculating $RBA = 0.8782 * IVBA - 0.028$ [46]. The EPA Method 1340 was updated in 2017 to use soil sieved to <150 μm, however the majority of our field and lab work was conducted prior to this EPA update and followed the previous method. Recoveries were within the expected range for NIST 2710a (96%, n=1), NIST 2711a (115%, n=1), a duplicate (98% recovery, n=1), and a matrix spike (92% recovery, n=1). For a subset of 13 samples contaminated by different industries analyzed in 2014, a 1:100 soil-to-solution ratio was maintained by using 0.2 g soil in 20 mL glycine solution, instead of the standard 1 g in 100 mL, and a hot water bath on a shaker table was used instead of the incubator.

1.3.6 Statistical analysis

Statistical analyses were performed with R Studio 1.0.136 using R 3.2.3 (R Core Team 2015) to assess the difference between (a) the XRF and ICP-MS Pb results for extracts, and (b) the field procedure extracts and the Drexler and Brattin (2007) IVBA extracts. Since the data are not normally distributed, we used a Spearman's rank correlation coefficient. Correlation between data sets were considered not statistically significant if $p>0.05$.

1.4 Results

1.4.1 XRF analysis of field procedure extracts

A total of 114 liquid samples were analyzed by both ICP-MS and XRF, including 5 Pb-solution standards and the field-procedure extracts from a subset of 107 soil samples and 2 NIST soil standards. Concentrations of Pb determined by XRF after blank correction were consistent with ICP-MS analyses across a range from <0.1 to 930 mg/L (Spearman's r_s= 0.99, $p<0.001$). The XRF analyzer overestimates Pb concentrations in the glycine solution by about 16% (Figure 1.2).

1.4.2 Field procedure extracts

The concentrations of Pb extracted by the field procedure and the original Drexler and Brattin method for 52 soil samples are well correlated (Spearman's r_s= 0.92, $p < 0.001$) (Figure 1.3). Across the range of concentrations and contamination types, the field procedure extracted about one third as much Pb (mean 37±15% SD, range 4-73%). The 3 soil samples from a smelter in India are outliers for which the field procedure extracted 70% of the Pb extracted by Drexler and Brattin method (Table 1.1). The amount of Pb extracted was corrected for the dilution of the soil into solution by weighing the soil for both methods. However, no large difference is seen in the best-fit line across the subset of samples that

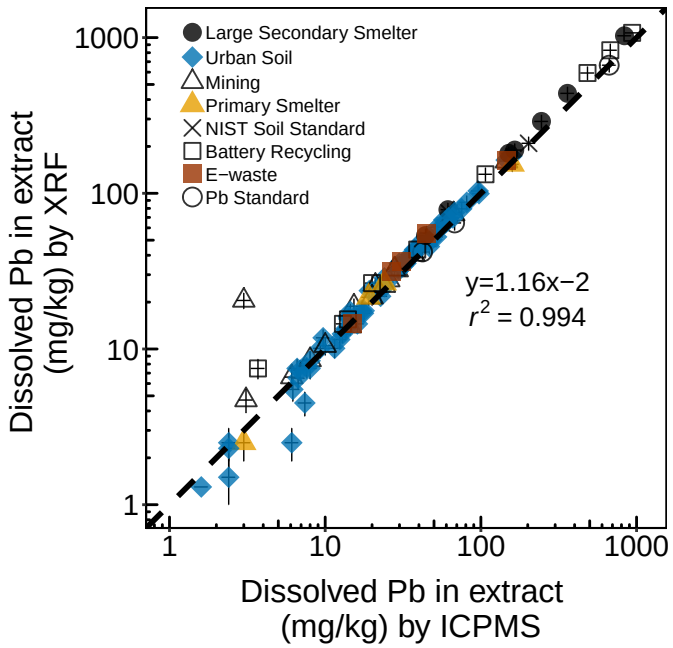

Figure 1.2: Blank-corrected XRF vs. ICP-MS measurements of dissolved Pb (mg/kg) in solution for the field-procedure extracts of 107 soil samples and 2 NIST soil standards as well dissolved Pb standards. XRF and ICP-MS error bars are 10%. Samples with <10 mg/kg Pb by XRF were analyzed again tripling the analysis time per beam energy. One non-detect sample by XRF is plotted at 1.2 mg/kg, half the instrument's estimated detection limit. Different types of contamination are shown in the legend.

contained both soil weight and scoop volume (Figure A.4).

Total soil-Pb concentrations in the 137 soil samples from different countries and 2 NIST soil standards measured by XRF ranged from 40 to 100,000 mg/kg (Figure 1.4). The field procedure extracted between 12 to 10,700 mg/kg Pb from these same samples. Thirty-one solutions from the field procedure were checked by a pH test strip, of which 28 confirmed the pH remained below pH=2, and three indicated the pH was between 2 and 3. The field procedure extracted the highest proportion of Pb from soils around large secondary smelters, followed by soil near used lead-acid battery recyclers, e-waste sites, NYC urban areas, a primary ore smelter, and mining areas (Table 1.1).

1.4.3 Color readings

Lead concentrations in 79 field procedure extracts (65 urban soil samples from New York City and 10 mining-impacted soils from Peru) were ranked as high/medium/low based on

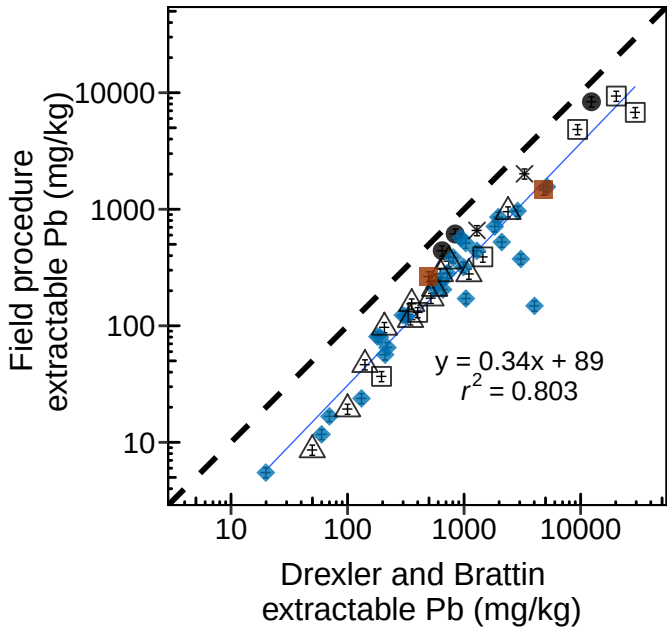

Figure 1.3: Amount of Pb extracted by the field procedure and the original Drexler and Brattin method for n=52 soil samples (including 2 NIST standards) after accounting for soil-to-solution dilution. Extracted Pb was analyzed by ICP-MS and error bars are 10%. Samples from large secondary smelters, battery recycling, and e-waste were analyzed by the early procedure, which maintained the 1:10 and 1:100 soil-to-solution ratios but used less soil. For the 1:10 field procedure method 1g soil was added to 10 mL of a glycine solution, and for the 1:100 bioaccessible Pb method 0.2 g soil was added to 20 mL of a glycine solution. Symbols indicating contamination type are the same as in Figure 1.2.

the intensity of the purple color after 5 minutes and the amount of precipitate after 24 hours (Figure 1.5). After 5 minutes, all 23 samples that ranked high extracted more than 200 mg/kg Pb, and all 38 samples that ranked low extracted less than 220 mg/kg Pb. The detection limit is reduced after 1 hour, as 33 samples ranked high and all had extracted more than 150 mg/kg Pb (Figure A.3). Of the 34 samples ranked low, 31 extracted less than 150 mg/kg Pb. Assessing the amount of precipitate formed after 24 hours further reduced the detection limit: all 38 samples that ranked high extracted more than 150 mg/kg Pb, and all 29 samples that ranked low extracted less than 140 mg/kg Pb.

To compare the amount of Pb extracted by the field procedure to EPA soil standards, federal total Pb soil screening levels were converted to bioaccessible Pb concentrations, where $IVBA_{EPA} = (0.6{+}0.028)/0.8782 = 71.5\%$, with the EPA's assumption of 60% (0.6) RBA (or 30% ABA) [46, 47]. At 71.5% IVBA, the EPA soil screening levels of 400 and 1200 mg/kg

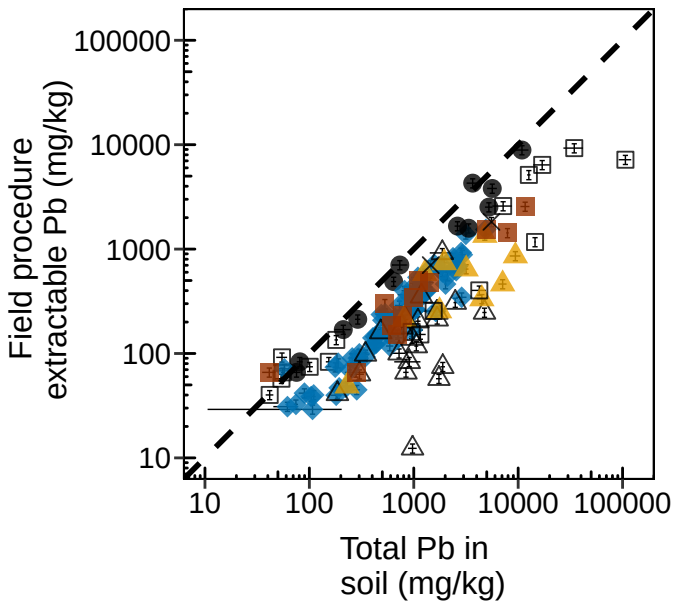

Figure 1.4: Concentration of Pb extracted by the field procedure for 139 soil samples of varying contamination types (symbols as in Figure 1.2). Total Pb in soil was analyzed by XRF and error bars are the standard deviation of 3 measurements. Extracted Pb was analyzed by XRF and blank and slope corrected based on the equation in Figure 1.2; also shown are 10% error bars.

total Pb convert to 286 and 858 mg/kg Pb extracted by the Drexler and Brattin IVBA method. These levels were then converted to the Pb that field procedure would extract by using equation from Figure 1.3, resulting in 190 and 387 mg/kg Pb, respectively.

Comparing the visual color rankings to these reference levels, we see that after 5 minutes, samples that extracted more than 387 mg/kg Pb ranked either medium (n=2) or high (n=18), while samples that extracted less than 190 mg/kg Pb ranked either low (n=36) or medium (n=2) (Figure 1.5). After 24 hours, all samples extracting more than 387 mg/kg Pb ranked high (n=20). Of the 38 samples extracting <190 mg/kg Pb, a larger fraction ranked medium (n=8) and high (n=1) due to the lower detection limit.

Table 1.1: Proportion of Pb extracted by the field procedure compared to the original Drexler and Brattin (DB) method (See Figure 1.3) and Proportion of total soil-Pb extracted by the field procedure (See Figure 1.4).

	% Pb extracted by the field procedure compared to DB		% total soil-Pb extracted by field procedure	
contamination type	mean(%) (±1SD)	n	mean(%) (±1SD)	n
large secondary smelter	70 (±3)	3	78 (±21)	12
urban soil	33 (±12)	27	34 (±14)	65
mining soil	35 (±1)	12	17 (±12)	21
primary smelting			22 (±13)	10
battery recycling	33 (±13)	6	53 (±46)	17
e-waste	42 (±16)	2	42 (±38)	12
standards	56 (±7)	2	41 (±11)	2
total	37 (±15)	52	78 (±20)	139

1.5 Discussion

1.5.1 Tradeoffs between field and laboratory testing

The field procedure and the Drexler and Brattin method produced remarkably consistent results even if only about one third as much Pb was extracted by the field procedure (Figure 1.3, Table 1.1). Likely reasons that the field procedure releases a lower fraction of total Pb include the following: larger particle size (∼1 mm instead of <250 μm or 150 μm), readsorption due to the higher soil-to-solution ratio (1:10 vs. 1:100), lower extraction temperature (22°C to 37°C), and possibly less frequent shaking. Reducing the soil-to-solution ratio from 1:100 to 1:10 is crucial, however, for reaching a Pb concentration in solution that is high enough to (a) form a color precipitate with sodium rhodizonate and (b) analyze the extract solution by XRF. It would be impractical for a wide group of users in the field to follow the Drexler and Brattin method, which stipulates sieving soil to <250 μm, or the updated EPA 1340 method, which sieves soil to <150 μm. Similarly, using ambient temperature (10-30°C) instead of an incubator set to 37°C is a requirement for adapting the method for use in the field. Another simplification is that the field procedure relies on a volumetric method, a small scoop, to measure the amount of soil added to glycine solution.

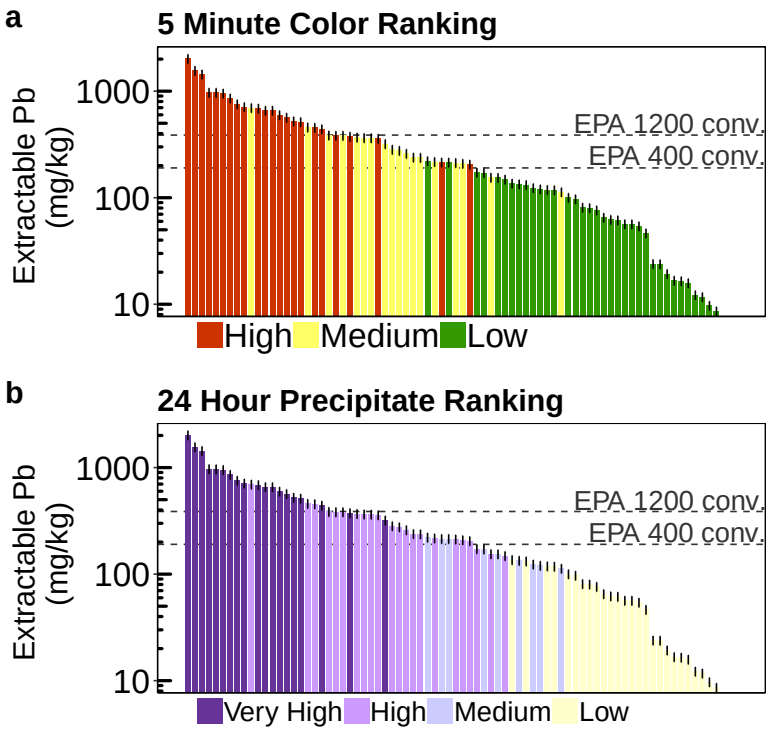

Figure 1.5: Ranking of field procedure extracts by extractable Pb concentration (dissolved Pb measured by ICP-MS and multiplied by dilution factor) after (a) 5 minutes based on color and (b) 24 hours based on precipitate amount. Rankings are compared to EPA soil screening levels of total Pb converted to the amount of Pb extracted by the field procedure based on 71.5% IVBA and the equation in Figure 3 (400 $\rightarrow$ 190 and 1200 $\rightarrow$ 387 mg/kg Pb).

The density of soil can vary widely, however; the mass of 3 scoops of dried soil analyzed for this study ranged from 0.5 to 2.8 g (mean 1.6$\pm$0.4 g, $\pm$1 SD). However, across the subset of samples that contained both soil weight and scoop volume (Figure A.4), the field procedure still extracted a similar proportion of Pb. When increased accuracy can be obtained with an XRF analyzer, bringing a portable balance to the field for maintaining a more consistent soil mass could be justified. Finally, although the pH didn't increase much in these samples, a pH test is also recommended to confirm that the pH of the field-procedure extract remains around or below 2, especially when testing soils with a high pH buffering capacity. Site-specific confirmation of pH stability and average scoop mass could be a simple way to increase accuracy without measuring these parameters on all samples.

Results from the simplified field procedure admittedly may be less directly relatable to

child exposure, or at least the relationship established between absorption of Pb in juvenile swine and the Drexler and Brattin procedure [46]. Larger particles, for instance, are less likely to stick to hands and be ingested. Such limitations are more than compensated, in our opinion, by the benefit of providing concerned parents or community members with the means of testing soil wherever a child is likely to play. Furthermore, the field procedure outlined here still manages to give a reasonable estimate of bioaccessible Pb in soils, which may be a better measure of actual health risk from Pb in soil than total Pb measured by XRF in bulk soil. The current thresholds of <200, 200-400, and >400 mg/kg bioaccessible Pb in soil could be adjusted if needed by varying the amount of soil added to the extraction solution. However, these values do not differ greatly from the calculated 190 mg/kg and 387 mg/kg field procedure extractable Pb that correspond to the current EPA screening levels of 400 and 1,200 mg/kg total soil Pb.

The field procedure estimates bioaccessible Pb by measuring the concentration of Pb released into the extract, which is directly related to health risk. Results from the field procedure are therefore sufficient to start prioritizing and addressing the most hazardous areas. Since soil contamination is often very spatially heterogeneous, once the location of Pb hotspots is known, individuals and communities can avoid these areas and take additional actions to reduce exposure. Possible actions include covering the area with clean soil or another barrier, ensuring children do not play in the high-Pb area, ensuring high-Pb soil is not transported out of the area or into homes, and maintaining clean environments with low dust and dirt levels where children play and eat [44, 53].

1.5.2 Extension of the method

In addition to identifying areas of hazardous Pb in soil with the colorimetric method, the field procedure could be used to estimate IVBA as described by Drexler and Brattin [46] and EPA Method 1340 [50] by measuring the Pb in the field-procedure extract solution by XRF or ICP-MS and estimating the Pb extracted by the Drexler and Brattin (DB) method

by $Pb_{DB} = (Pb_{Field-procedure} - 89)/0.34$ (Figure 1.3) and applying corrections to the XRF readings if needed (Figure 1.2). One could consider developing a site-specific or updated relationship, especially if samples are from soils near large secondary smelters or unknown types of contamination (Table 1.1).

Pairing the field-procedure extraction with an XRF in the field could also help select samples for more detailed laboratory analysis. In situations where laboratory analysis is not planned or available, local health departments or technicians with access to a portable hand-held XRF analyzer could still assess the health risk of soil Pb contamination more accurately by applying the field procedure than by only measuring total-Pb concentrations. One would need to measure the total-Pb concentration in the soil in order to determine the proportion of soil Pb that is bioaccessible.

1.5.3 Potential color interference

Our observations show that in addition to analyzing the color at 5 minutes, waiting for 24 hour to assess the amount of precipitate amount enables us to confirm the presence of Pb and lowers the detection limit. When glycine extracts turn brown, blue, or gray instead of purple, they should be categorized as medium and analyzed for the presence of precipitate after 24 hours. While the use of sodium rhodizonate to detect Pb has been well documented, Feigl and Suter (1942) point out that complexes are formed with other cations including zinc (brown-violet), tin (violet), strontium (red-brown), barium (red-brown), cadmium (brown-red), mercury (brown-red), bismuth (red-brown), calcium (red-brown), and iron (blue) [64]. We tested the following solutions for potential interference: zinc (30 mg/kg and 1000 m/kg), barium (30 mg/kg), copper (30mg/kg), calcium (30 mg/kg), and iron (30 mg/kg and 500 mg/kg), created from high-purity standards in 1-2% nitric acid for ICP-MS. Only iron (Fe) solutions resulted in a potentially interfering dark solution, although this solution was dark blue and not purple; all other solutions remained light yellow in color.

To further check for the likelihood of these interferences in our soil extracts, we examined

elemental concentrations of these elements in the extract solutions. Besides Pb, the only element detected by XRF that was significantly correlated with the color ranking of our samples was zinc (Zn). Extract solutions from two Peruvian mining samples contained 2700 and 1500 mg/kg Zn; all other samples contained <300 mg/kg Zn. While the two samples with >1500 mg/kg Zn were a darker, brown color at 5 minutes, the presence or absence of a precipitate after 24 hours accurately indicated the level of Pb. The Zn standard of 1000 mg/kg had not shown any color change. The Fe standard of 30 mg/kg had turned blue; however all our extracts contained Fe below the XRF detection limit of 15-20 mg/kg.

1.6 Conclusion

Screening soils for Pb is not common in residential areas and urban gardens, neither in the U.S. nor internationally, although the negative health impacts of Pb are well established and many studies have shown elevated Pb levels in soils, often due to historical contamination. As studies continue to confirm negative health impacts at lower Pb exposures in children and cardiovascular impacts later in adults [8, 14], testing soil for Pb is likely to receive more attention, especially in urban and previously industrial areas. The cost of materials and supplies per analysis of the current procedure is around US$5 per sample. This could be reduced significantly if a kit derived from the procedure is produced in large quantities. Due to its modest cost and simplicity, the field procedure is well suited for deployment by local health departments, citizen scientists, concerned parents, or community groups without access to a laboratory.

1.7 Acknowledgments

Some of the early work on the field procedure was conducted by Carolina Bravo and Sheila Xiah Kragie while students at Columbia University. We thank the Pure Earth team for providing contaminated soil samples from various countries in 2013. Dr. Johny Ponce from

the Center for Research in Environmental Health in Peru facilitated the soil sampling in Peru 2015-2017. This research was partially supported by a seed grant from the Earth Clinic of the Earth Institute at Columbia University and NIEHS SRP grant P42 ES010349.

Chapter 2

Does involving parents in soil sampling identify causes of child exposure to lead? A case-study of community engagement in mining-impacted towns of Peru

This chapter is published in GeoHealth.[1]

2.1 Abstract

Over a million people in Peru may be exposed to lead (Pb) due to past or present mining-related activities, however neither soil Pb nor blood Pb are routinely monitored throughout the country. Because little is known about Pb contamination in smaller mining-impacted towns, soil Pb was mapped in four such towns with a portable X-ray fluorescence (pXRF) analyzer in 2015. The roadside mapping delineated hotspots of highly contaminated soil (1,000-6,000 mg/kg Pb) in two of the towns. The local health department, provided with a LeadCare II analyzer, then measured blood-Pb levels >5 μg/dL in 65% and >10 μg/dL in 15% of children (n=200) up to 6 years of age in these same four towns. There was no clear relation between child blood-Pb levels and Pb levels in soil samples collected inside

[1]Franziska C. Landes, Jennifer Inauen, Johny Ponce-Canchihuaman, Kathie Markowski, Tyler K. Ellis, Alexander van Geen, "Does involving parents in soil sampling identify causes of child exposure to lead? A case-study of community engagement in mining-impacted towns of Peru." *GeoHealth*, August 8, 2019. https://doi.org/10.1029/2019GH000200

(n=50) or outside the home (n=50). Increased child blood Pb was associated with decreased level of cleanliness of parent clothing and shoes, linking a possible behavioral factor for transferring contaminated soil and dust to children. In order to explore individual exposure and variations in soil Pb, ten parents of children with blood Pb >10 μg/dL and ten parents of children with blood Pb <5 μg/dL were invited to collect soil samples in areas where their children play and screen it for Pb using a color-based field procedure. Importantly, parents identified a new hotspot of Pb contamination that had been missed by the previous pXRF soil mapping. The findings highlight the feasibility and value of involving families impacted by environmental contamination to identify and reduce environmental health risks.

2.2 Plain language summary

While many people in Peru live near sites of mining activities, few realize these places put them at risk of exposure to lead, a toxic heavy metal. This study sought to determine if it was possible to involve parents in sampling and testing soil for lead as a potential way of increasing awareness and reducing exposure. Our team of researchers first tested soil for lead using a portable instrument in four small towns affected by mining. We found areas with high levels of lead three to fifteen times above the U.S. standard for soil where children play. The local health department found that blood lead levels in 30 out of 200 children exceeded the Peruvian standard and 130 exceeded the U.S. reference level. While we found no clear relationship between blood lead levels in children and lead levels in soil, the data do show that cleanliness of parent clothing and shoes reduces child exposure to lead. Twenty parents then collected and tested soil where their children play using a color-based field test and found a new area of contamination. This form of community engagement in environmental could be expanded to other mining areas and even other environmental health risks.

2.3 Introduction

The toxicity of lead (Pb) is widely recognized; lead has been linked to childhood neurological impairment [3–6] and cardiovascular disease later in life [8, 13]. Children under the age of 6 are at highest risk of Pb exposure as they explore their environment by crawling on the ground and placing dusty toys and hands into their mouths. Children show reduced test scores and greater risk of learning disabilities even at blood lead levels (BLL) previously considered safe [5]. To reflect this, the U.S. Centers for Disease Control and Prevention (CDC) in 2012 replaced its BLL standard of 10 μg/dL with a reference level of 5 μg/dL. This reference level is based on the 97.5th percentile of children tested in the 2010 National Health and Nutritional Examination Study (NHANES). Because exposure in the US continues to decline, this reference level would have to be updated to 3.5 μg/dL based on the 2015 NHANES [12, 14, 15].

Child BLLs have been associated with soil-Pb levels [28, 29] and resuspended Pb in air [26, 30]. A pooled analysis by Lanphear et al. (1998) of 12 studies found Pb loading in house dust, collected by wipe method (mass per area) was the major contributor to BLL in children age 6 to 36 months. Soil-Pb concentrations also predicted child BLL levels in this study as did age, mouthing behaviors, and race. Indoor dust-Pb loading also contributed more to child BLL than soil Pb. Child BLLs, which peak in summer months, have been linked to soil Pb through atmospheric conditions and the resuspension of soil Pb into the air, with children age 2 and younger the most impacted [30]. The review by Mielke and Reagan (1998) of studies with BLL and possible contributors of air, dust, soil, water, food, and paint demonstrated that 42 of the 46 studies with soil-Pb information found a positive correlation between BLL and soil Pb. An analysis in Bunker Hill, an old smelting and mining area in Idaho, found that home-soil and neighborhood-soil Pb levels were most related to BLLs of younger children, while community-wide soils had the largest impact on BLL overall and were highest for children 5 to 6 years old [52].

While BLLs in the U.S. have dropped precipitously from 99.8% $>$ 5 μg/dL (1976-1980)

[16] to 0.5% (2013-2014) [15], Pb poisoning is still a major health issue throughout many low- and middle- income countries (LMICs) [4, 17]. In Peru, for instance, the Ministry of Health tested 233 children in the mining city of Cerro de Pasco in 2005 and found BLLs in 86% of children > 10 μg/dL and 22% > 20 μg/dL [70]. Elevated BLLs are likely found throughout Peru: a national assessment calculated that 1.6 million people live within 5 km of an active mine, former mine, ore processor, or smelter [40]. Testing conducted in 2014 in the smelter town La Oroya found BLLs in 58% of 335 children > 10 μg/dL [71]. Other studies in Peru have found BLLs associated with traffic levels in police officers [72] and mineral ore storage in Callao [73–75].

Although the more infamous cases of Pb contamination in Peru have been described in cities like Cerro de Pasco [76], La Oroya [77], and Callao [74], little is known about smaller towns that are also impacted by Pb-contaminating industries such as smelting, mining, or battery recycling. Many such towns neighbor the larger industrial centers or are situated along the major transportation routes for ore concentrates. In this study, we investigated the extent of soil-Pb contamination in four of these smaller potentially impacted towns in the Huarochiri Province of central Peru with a roadside mapping by X-ray fluorescence. The results showing two areas highly contaminated with Pb were presented to community members and municipalities. A group of local parents was then trained to collect soil samples in areas where their children play and they participated in the screening of their soil samples for Pb using a simple test. We show that local participation proved to be valuable because sampling by parents revealed a previously unidentified contaminated area. We also explore possible associations of soil, dust, and survey results obtained as part of the study with child BLLs obtained by the local health department.

2.4 Materials and methods

All protocols involving human subjects research were approved by the CU Institutional Review Board (IRB) and the Peruvian IRB board, PRISMA. The project was also presented to and endorsed by the local municipalities and health centers. Fieldwork was conducted with the local not-for-profit organization Center for Research in Environmental Health (CREEH) based in Lima, Peru. We regularly met with local health departments and municipalities before, during, and after the soil sampling.

2.4.1 Instrumental analysis

Surface soil samples were analyzed in situ with a portable, X-ray fluorescence (XRF) instrument (InnovX Delta Premium) and ex situ with a benchtop stand for the instrument. For ex situ analysis, sieved samples (<1mm) in 20 mL scintillation vials were sealed with plastic wrap and inverted on the XRF. Analysis time in the benchtop stand was 20 seconds at each of three incident-beam energies in the instrument's standard soil mode. When measuring soil in situ in the field, the analysis time was reduced to 10 seconds per incident beam. Filtered soil extracts as well as home soil and/or dust samples were also analyzed by the XRF in the benchtop stand.

X-ray fluorescence is increasingly used to screen soils, as in EPA Test Method 6200 [69], because of its low cost per sample when compared to acid digestions and mass spectrometer analysis, and the soil-Pb results correlate highly with digest results [67, 68]. In this work, the XRF's internal calibration and data reduction was confirmed by repeat analysis of Standard Reference Material soils from the U.S. National Institute of Standards and Technology (NIST) with high (5,532 mg/kg Pb in NIST 2710), medium (1,162 mg/kg Pb in NIST 2711) and low (18.9 mg/kg Pb in NIST 2709) concentrations of Pb. The XRF results were within 10% of NIST published values for standards 2711 (n=55) and 2710 (n=8). The XRF overestimated, on average, the 18.9 mg/kg from NIST 2709 (n=7) as 22.9 (120%) mg/kg.

Recent work has shown that XRF analysis of Pb in liquid extracts highly correlates with analysis by inductively coupled plasma mass spectrometer (ICP-MS) [78], which was also seen for samples analyzed in the present study (Figure B.1). Concentrations of Pb in water samples were analyzed in the laboratory by high-resolution ICP-MS (Thermo Scientific Element II); all field-procedure extracts were also analyzed by ICP-MS for confirmation. The ICP-MS procedure was verified by analyzing NIST reference materials 1640A (n=15), which was within 6% of its published value of 12.101 μg/L Pb, and 1643F (n=15), which was within 12% of its published value of 19.63 μg/L Pb. All ICP-MS dilution and vial blanks contained <1 μg/L Pb.

2.4.2 Site description

The study took place in the four neighboring towns of Corcona, Carachacra, Cocachacra, and Tornamesa approximately 40 to 60 km east of Lima (-11.914°W, -76.546°S) at an elevation of 1400±150m. The sequence of four towns follows a narrow valley along the railroad and the Carretera Central, the main highway connecting the smelter town of La Oroya to the port of Callao, north of the capital of Lima (Figure 2.1). These four towns were chosen due to their location along this major thoroughfare, based on the assumption that railcars and trucks carrying mineral ore concentrate provided a possible source of Pb contamination. In addition, on the eastern end of Corcona, approximately 50 km east of Lima, volcanic-hosted massive-sulfide deposits were mined for barite ($BaSO_4$), galena (PbS), pyrite (FeS_2), sphalerite ((Zn,Fe)S), and chalcopyrite ($CuFeS_2$). Mining of barite deposits peaked in the late 1970s, and mining of Zn and Pb deposits increased in the early to mid 1980s [79]. The study area receives only 250 mm of rainfall annually, leading to dry conditions favorable for soil resuspension.

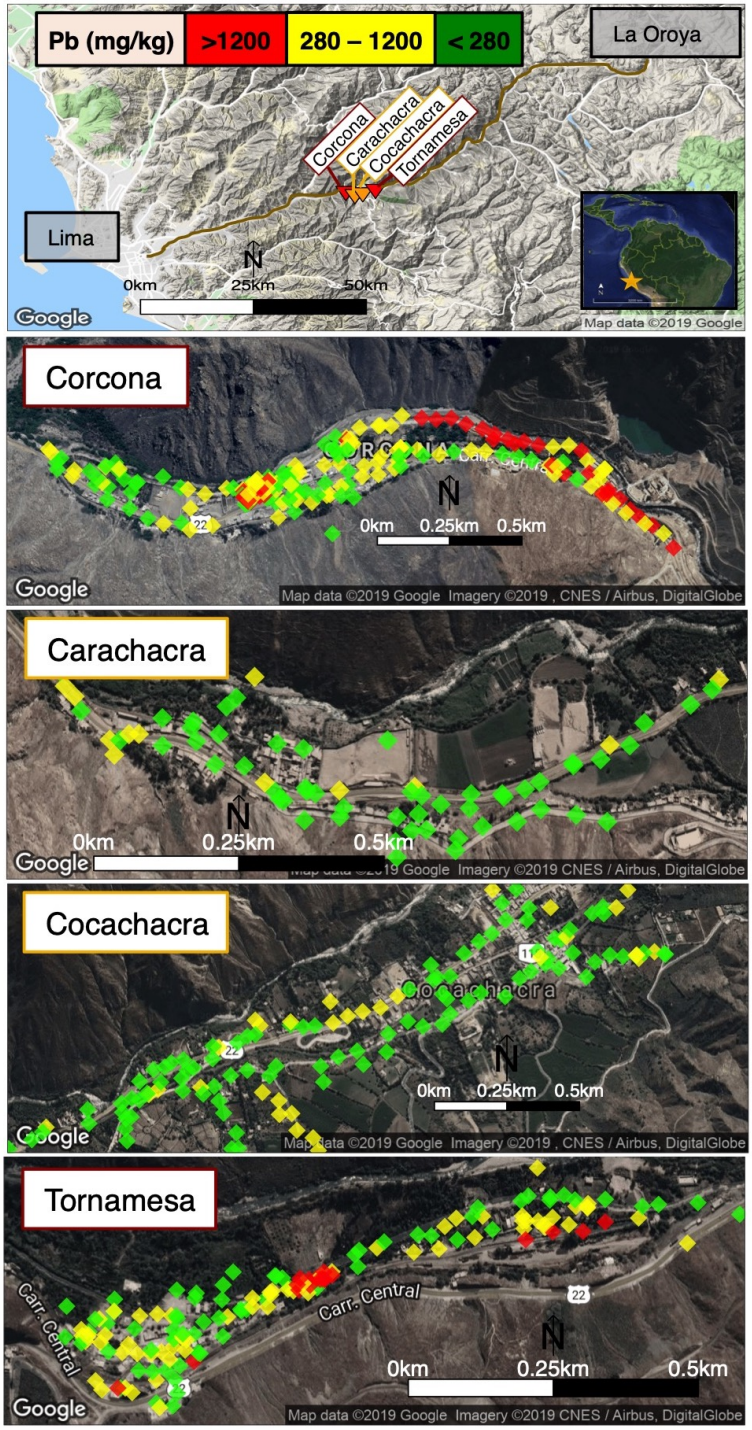

Figure 2.1: Study location in Peru, 40 to 60 km east of Lima. Soil sample locations of roadside XRF mapping are shown in the four towns and total-Pb concentration as measured by XRF are indicated in green (<280 mg/kg Pb), yellow (280-1200 mg/kg Pb), and red (>1200 mg/kg Pb). The threshold of 280 mg/kg Pb was chosen based doubling the Peruvian soil standard of 140 mg/kg.

Table 2.1: Participant characteristics (n=137) collected during Survey 1.

	%		Mean (SD)
Gender (woman)	91	Age	33.8 (9.2)
Literacy (literate)	97	Children	2.1 (1.2)
Secondary school or higher	85	Children (<6 years)	1.3 (0.5)
Participant or spouse works near mining	22	Monthly expenses (USD)	211 (127)
Other family member works in mining	38	Monthly income (USD)	380 (216)
Participant employed outside the home	33		

2.4.3 Local interviews / surveys

In July 2015, CREEH staff trained five interviewers to survey adult primary caregivers, hereafter referred to as parents, of children 6 years old and younger (Figure 2.2, Table 2.1). After posting flyers throughout the 4 towns, potential participants were contacted door-to-door. Interviewers surveyed 149 parents in July (Survey 1), and revisited 137 eight weeks later (Survey 2), approximately four weeks after a community meeting. As far as we can tell, we contacted all parents of children under 6 years of age who were at home during Survey 1. We were unable to find a complete list of parents; the best records were from the governmental Vaso-de-Leche (glass of milk) program, which didn't include higher income families. The survey included questions about the health impacts of Pb exposure, possible locations of Pb contamination, demographic information, questions assessing exposure-relevant behaviors, and factors that could impact those behaviors [80]. Interviewers also recorded observations such as children playing on the floor and appearance of cleanliness.

2.4.4 Home soil samples

With permission from participants, interviewers collected home dust or soil samples using a small dustpan and broom in the interior entryway of the house, or if this area was too clean, in another room (indoor home samples) during Surveys 1 and 2 conducted in July and September 2015, respectively. If it was not possible to collect sufficient material for

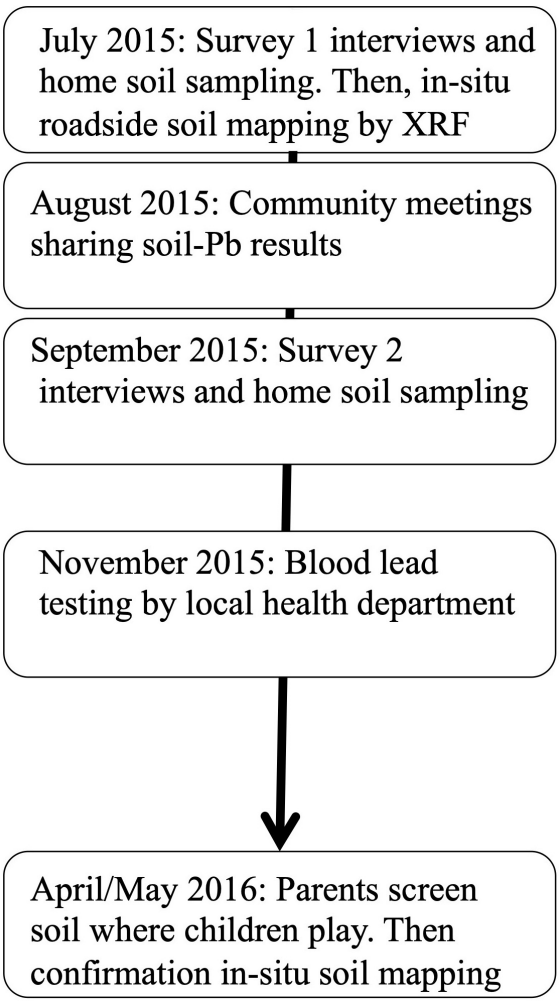

Figure 2.2: Study timeline from 2015 to 2016 including interview surveys, home soil sampling, roadside soil mapping by XRF, and parent soil screening.

analysis indoors, a soil sample was taken from just outside the front doorstep (outdoor home samples). Parents were asked the location of the sample from Survey 1 to determine the sample location during Survey 2. All home samples were sieved through a 1 mm sieve into 20 mL scintillation vials and analyzed by XRF.

In Survey 1, home samples were collected from 145 households, and 138 contained enough material ($\sim$1 g) for analysis by XRF (n=54 indoor, n=49 outdoor, and n=35 unknown). During Survey 2, 139 home samples were collected, and 136 were analyzed (n=50 indoor, n=68 outdoor, and n=18 unknown). Only 24 samples were confirmed to have been collected indoors both times.

2.4.5 Roadside soil mapping

Soil-Pb concentrations were mapped in situ in July 2015 using the portable XRF analyzer in approximately 60 m intervals along publicly accessible roads, pathways, parks, and railroad tracks. In 2016, we conducted additional XRF mapping where parents found a new hotspot (n=37) and near homes not reached in 2015 (n=23). The 2016 data expanded the coverage of the towns but also over-represented the most contaminated areas.

2.4.6 Water samples

At the request of the local community, 16 water samples were collected from drinking- and non-drinking water sources. Scintillation vials were rinsed three times in the source water before collecting a 20 mL sample. Once in the lab, samples were acidified along with blank vials filled with MQ water. In August water samples were collected in duplicate and one was filtered through a 0.45 μm nylon syringe filter. All ICP-MS method and vial blanks contained <1 μg/L Pb and all vial blanks contained <0.1 μg/L.

2.4.7 Community meeting

We presented information about soil-Pb contamination and the health impacts of Pb at community meetings in each of the four towns. Central to these meetings was the presentation of a poster-sized (2 m by 1 m) map of soil-Pb levels in each town based on the roadside XRF mapping (Figure 2.1). Participants received a handout copy of the map (size A4) with key information discussed on the back. The map was posted in a central location in each town. In addition, in Corcona and Tornamesa, the towns with a hotspot of soil Pb > 1,200 mg/kg, two more posters were placed near the main entry points to the contaminated areas.

The soil-Pb maps were created in Google Earth, with colored pins indicating three health-risk categories based on total-Pb concentrations: low in green (<280 mg/kg Pb), medium in yellow (280 to 1,200 mg/kg Pb), and high in red (> 1,200 mg/kg Pb) (Figure 2.1). The 280

mg/kg Pb in soil threshold was set by doubling the Peruvian residential soil standard of 140 mg/kg [81]. For comparison, the U.S. EPA's soil hazard standard for bare soil in children's play areas is 400 mg/kg and for other residential areas is 1,200 mg/kg [39]. The map also included the recommendations in Spanish to "protect your child - avoid contaminated areas," and advised, in high-risk areas, "do not let children touch the contaminated soil," and in medium risk areas "avoid that your children play on the ground," and "avoid bringing this dirt to your home."

The local municipalities provided the meeting space and informed residents about the meeting details. Such collaboration will be key for any future expansion of a soil-Pb testing program. However, various delays in communication left little time between when the meeting was announced and when it took place. Even in the town where the mayor personally knocked on doors the morning of the meeting, only 4 of the 26 attendees were among the 19 participants in the study.

2.4.8 Blood lead levels (BLL)

After reviewing the soil-Pb data in late 2015, the local health department (Dirección Regional Salud Ambiental - DIRESA) offered parents a blood-Pb test for children six years old and younger. Health department workers were provided with a LeadCare II unit that they used to measure Pb in a small pin-prick sample of blood with detection limit of 3.3 μg/dL [82]. The instrument is widely used for Pb monitoring across the US because it can be used in non-specialized doctor's offices that are not regulated for laboratory analysis. Children with a BLL $>$ 9 μg/dL (n=44) were offered confirmation testing, and 33 children returned for a second LeadCareII BLL measurement. We received BLL information for children whose parents signed additional BLL-specific consent forms.

2.4.9 Field procedure to screen soil Pb used by parents

In late April 2016, 11 parents from Corcona and 9 parents from Tornamesa were invited to use a new field procedure to collect soil samples where their children play and screen them for Pb using a visual indicator (Figure B.2). The 20 consenting parents were selected based on the blood-Pb information of their children, provided by the health department, to capture soils where both the most exposed and least exposed children play. Parents attended a training session at the local health center to learn how to use the field procedure and borrowed a smartphone to record sample information.

Parents were asked to collect up to 6 soil samples: 3 from locations where their child currently played and 3 from alternative locations where their child could play. These alternative locations were included so that parents would already know of a safe alternative play area in case their current play area was determined to be contaminated. Parents collected the soil samples independently by sieving the soil through a basic kitchen sieve ($\sim$ 1 mm mesh) and funnel into a 20 mL scintillation vial. Using the SurveyCTO app [83], parents recorded geographic coordinates, a site photo, sample ID, and a brief description, occasionally with help from a family member or CREEH field staff. This information was stored by the app on the smartphone, without cellular connection, until it was uploaded to a central database by connecting to a wireless internet or cellular hotspot.

After collecting the soil samples, parents met with a researcher to analyze the samples using an earlier version of the field procedure for hazardous Pb described by Landes et al. [78]. This method is based on the 0.4 M glycine extraction (pH=1.5) of Drexler and Brattin [46] and the U.S. EPA's standard bioavailability method for Pb [47, 50]. Parents were asked to add a small spoonful of soil (approximately 1 g) to 10 mL of the extraction solution in a scintillation vial and shake it for 30 seconds at least 45 minutes before meeting with a researcher. At the meeting parents shook the vial again for 30 seconds and allowed the soil to settle for 15 minutes, for a total extraction time of at least 1 hr. An aliquot of the extract was then decanted into the lid of the scintillation vial, and the tip of a white test

strip impregnated with sodium rhodizonate (Plumbtesmo® MACHEREY-NAGEL, #90602) was dipped into cap, allowing the liquid to rise via capillary action to 1 cm from the top.

The presence of Pb in the extract solution was determined by the color of the test-strip and, in some cases, also the direct addition of sodium rhodizonate. If the test strip turned purple, the extract contained a high concentration of Pb. Comparison with ICP-MS measurements had indicated that a purple test strip corresponded to >100 mg/L Pb in solution, or an equivalent of 1000 mg/kg extractable Pb in soil given the dilution ratio of 1 g soil in 10 mL solution. If the test strip turned light purple or speckled purple, the extract was classified as containing a medium concentration of Pb. In this case, or if no color was seen, a toothpick tip of sodium rhodizonate powder was stirred into the cap with the decanted extract solution. The liquid visibly turned purple at concentrations > 40 mg/L Pb in solution, equivalent to 400 mg/kg extractable Pb in soil, thus confirming the presence of a mid-range concentration of Pb in soil. After the color analysis with the parents, the liquid extract was filtered through a 0.2 μm syringe filter into a clean 20 mL scintillation vial by a researcher and immediately analyzed by XRF in the benchtop stand. After the fieldwork was completed, the extract Pb concentration was confirmed by ICP-MS.

The main difference of the field procedure used in this study relative to the later version described in Landes et al. (2019) is that a test strip impregnated with sodium rhodizonate was inserted directly into the unfiltered solution after the extraction time of 1 hour instead of adding a gelatin capsule of sodium rhodizonate to the filtered extract [78]. The procedure was later modified because we noticed that the Plumbtesmo® rhodizonate strips degraded with temperature and sunlight. By the end of the week, a test strip that had been in the field would no longer turn purple as it had at the beginning of the week. Since the sodium rhodizonate added to the extraction solution with a toothpick tip continued working throughout the week, it appears that the Plumbtesmo® strips are more susceptible to degradation.

2.4.10 Statistical analysis

Statistical analyses were performed with R Studio 1.0.136 [84] using R 3.5.1 [85]. Since blood-Pb levels and soil-Pb concentrations were not normally distributed, Spearman's rank correlation coefficient was used. To check for significance between blood lead categories, we employed the package Tableone [86], a chi square test for categorical variables, and a Kruskal-Wallis test for non-parametric continuous data. Differences between groups are indicated on boxplots by letters, based on a Mann–Whitney U test.

2.5 Results

2.5.1 Town soil samples

Concentrations of Pb measured at 437 locations during the roadside mapping in July 2015 range from 20 to 6,400 mg/kg Pb (mean±1 standard deviation (SD): 500±750 mg/kg). The Pb levels in 44% of samples are above 280 mg/kg Pb, in 30% are above the U.S. EPA 400 mg/kg hazard standard for bare soil where children play, and in 10% are above the U.S. EPA 1,200 mg/kg hazard standard for other soil (Figure 2.3). The mapping identified two hotspots of soil Pb above 1,200 mg/kg: one in Corcona and one in Tornamesa (Figure 2.1). In Corcona the hotspot stretches for 1 km along a river levee and around an old mine visible in satellite images. In Tornamesa, the hotspot follows the railroad tracks for 0.2 km around a turntable. As a result, mean soil-Pb is higher in the two towns with an identified hotspot, Corcona and Tornamesa (760±90 and 680±80 mg/kg, ±1 standard error of the mean (SEM)), than in the other two towns, Cocachacra and Carachacra (240±20 and 200±10 mg/kg, ±1SEM)(Figures 2.1 and 2.3, $p<0.01$).

By adding soil-Pb information from 2016, including the samples parents collected and the additional in situ portable XRF mapping conducted to confirm high soil-Pb, town-level data is available for 586 soil samples. Of these samples, 51% are above 280 mg/kg, 37%

are above 400 mg/kg, and 13% are above 1,200 mg/kg Pb. With the additional data for Corcona, where parents detected an additional hotspot, the mean Pb rises to 920±80 mg/kg (±1SEM) while remaining essentially unchanged in the other towns: Tornamesa (660±60 mg/kg), Cocachacra (240±20 mg/kg), and Carachacra (200±10 mg/kg).

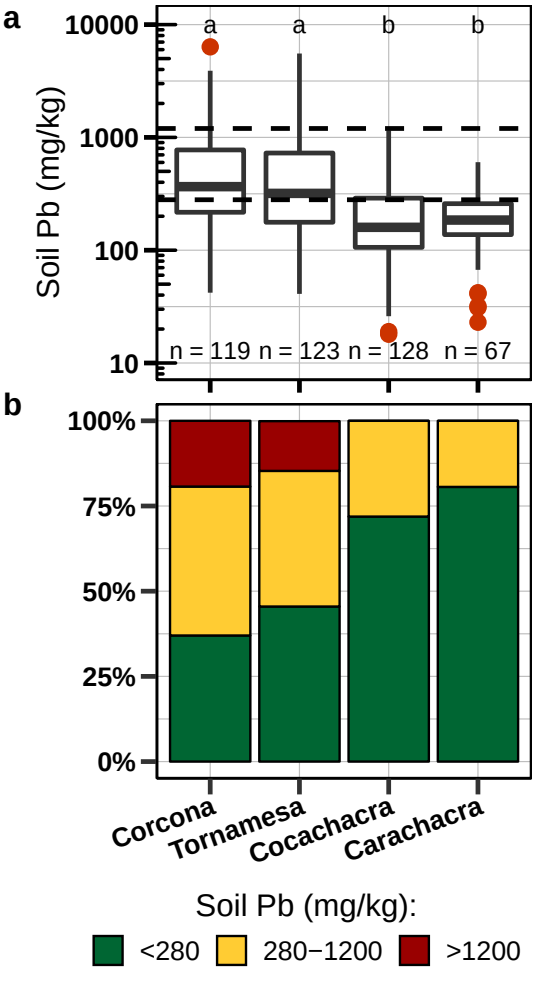

Figure 2.3: (a) Distribution of soil-Pb concentrations per town from the 2015 roadside XRF mapping. Box created from the lower hinge (25%), median, and upper hinge (75%). Whiskers extend to 1.5 × the inter-quantile range. (b) Proportion of samples per town below 280 mg/kg Pb, and above 1,200 mg/kg Pb. Different letters in (a) represent groups that are statistically different ($p<0.05$).

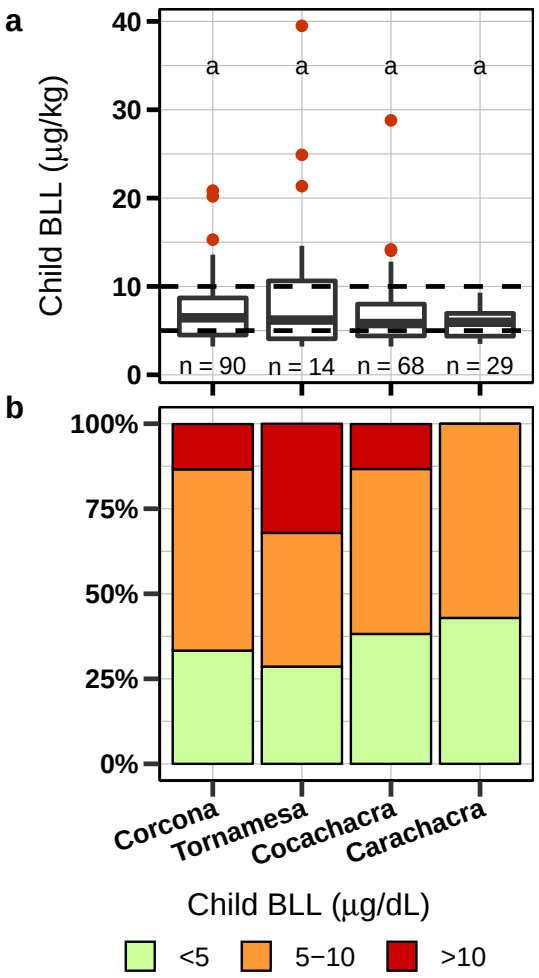

Figure 2.4: (a) Distribution of child blood Pb levels (BLL). Box created from the lower hinge (25%), median, and upper hinge (75%). Whiskers extend to 1.5 × the inter-quantile range. (b) Proportion of children with BLL over the reference levels of 5 and 10 µg/dL. Similar letters in (a) represent groups that are not statistically different ($p<0.05$).

2.5.2 Blood lead levels (BLL)

The arithmetic mean BLL measured in children across the four towns was 7.2±4.5 μg/dL (mean±SD) with a geometric mean of 6.4±1.6 μg/dL (±1 geometric SD (GSD)) (n=200) (Figure 2.4). Of these, BLL in 30 children (15%) were above 10 μg/dL, the Peruvian standard, and 130 (65%) were above 5 μg/dL, the CDC reference level. Of the 33 children tested twice, BLLs of 26 were confirmed above 9.0 μg/dL. The proportion of children with BLL >5 μg/dL varied from 57 to 71% across the towns. However, the proportion of children with BLL >10 μg/dL varied more noticeably between the towns with 13% in Corcona (n=90), 32% in Tornamesa (n=28), 13% in Cocachacra (n=68), and 0% in Carachacra (n=14). The arithmetic and geometric mean in these towns were, respectively, in Corcona, 7.1±3.4 μg/dL (±1 SD) and 6.4±1.5 μg/dL (±1 GSD), in Tornamesa, 9.2±8.0 and 7.2±1.9 μg/dL, in Cocachacra 6.8±3.9 and 6.1±1.6 μg/dL, and in Carachacra 5.9±1.8 and 5.6±1.4 μg/dL, and did not differ significantly (p=0.593).

2.5.3 Water samples

All water samples contain Pb concentrations below the Peruvian drinking water standard of 10 μg/L Pb and below the U.S. EPA Maximum Contaminant Level of 15 μg/L. All samples collected from drinking water taps, municipal springs or water sources contain less than 1 μg/L Pb. The highest Pb concentrations are in non-drinking water sources, in concrete drainages along the road both uphill from Cocachacra (5 μg/L Pb unfiltered) and in Tornamesa (1.6 μg/L Pb unfiltered); water samples collected from the Riomac River, accessed in Tornamesa, contain 1.0 μg/L Pb in the unfiltered sample. Total acid-dissolvable Pb concentrations in samples from a small creek running through Tornamesa are 3.0 μg/L (unfiltered) near the train tracks and, two-months later, 1.5 μg/L (unfiltered) and 0.4 μg/L (filtered).

2.5.4 Parent soil-Pb screening

Parents conducting soil screening with the field procedure identified 6 high-Pb samples, 5 of which contain >500 mg/kg extractable Pb measured in the field by XRF and correcting for dilution. Parents ranked 15 additional samples as medium, 13 of which contain >250 mg/kg extractable Pb. Average extractable-Pb concentration measured by ICP-MS for samples ranked high is 610±490 (±1SD) mg/kg (n=6), for samples ranked medium is 410±280 mg/kg (n=15), and for samples ranked low is 110±80 mg/kg (n=70). Average total soil-Pb concentration, measured by XRF, for samples ranked high is 1800±1240 mg/kg (±1SD), for samples ranked medium is 870±790 mg/kg, and for samples ranked low is 390±340 mg/kg.

The sampling and screening of soil conducted by parents revealed a new Pb hotspot. Three different parents collected high-Pb soil samples from the same neighborhood in 2016 in an area in western Corcona that our 2015 XRF mapping did not identify as a hotspot. We confirmed and delineated this new Pb hotspot with additional XRF measurements (mean soil Pb: 1800±1500 mg/kg, n=37, (±1SD)) (Figure 2.5). In addition, some parents collected samples near their work places, which included car wash areas. In one case follow-up in situ XRF mapping identified Pb concentrations up to 3,000 mg/kg, with average levels 900 mg/kg Pb (±180 SEM).

Across all samples collected by parents in areas where their children play, mean total soil-Pb concentration is 560±570 mg/kg (n=59, ±1SD), measured by XRF (median: 380, range: 20-3500 mg/kg). Similarly, the mean total soil-Pb concentration in alternative play areas is 580±760 mg/kg (n=32,±1SD, median: 360, range: 60-4200 mg/kg). For 11 parents, the mean total soil-Pb concentration collected in alternative areas is lower than 20% of the mean of samples collected in current play areas; for 6 it is higher than 20%. While median Pb-concentrations are below the U.S. EPA 400 mg/kg standard for both sets of samples, concentrations range widely.

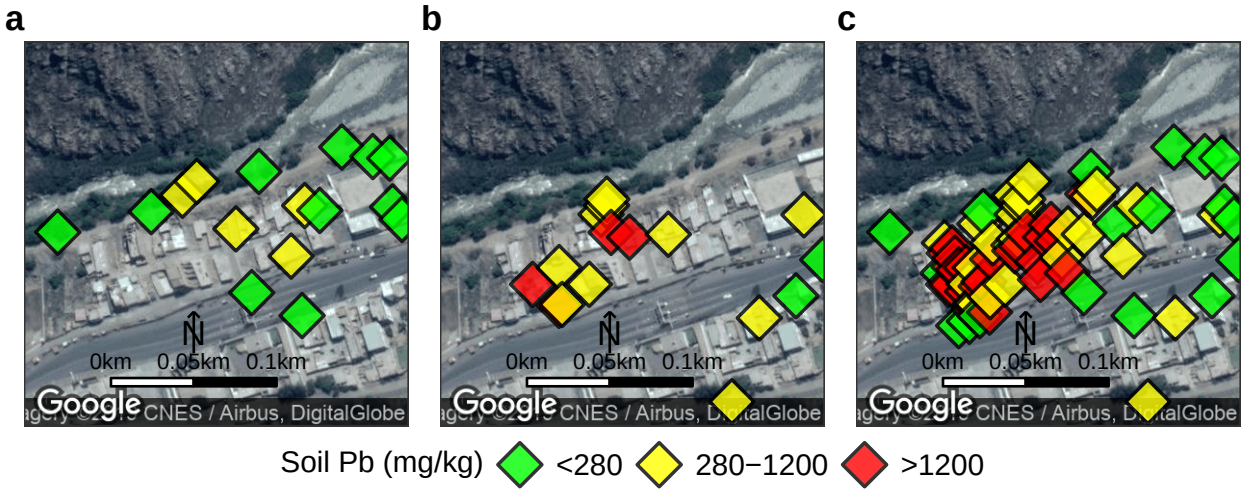

Figure 2.5: Progression from left to right of soil map for the area where parents identified a new hotspot by using a screening method for soil Pb. Pb concentrations are indicated by color in green (< 280 mg/kg), yellow (280-1,200 mg/kg), and red (> 1,200 mg/kg) for (a) roadside XRF mapping in 2015, (b) parent-collected soil samples in 2016, and (c) confirmation in situ XRF mapping with data from (a) and (b).

2.5.5 Proportion of extractable Pb

On average the field procedure extracted 38±29% (±1 SD, n=89) of the total soil Pb, after accounting for a soil-to-solution ratio of 1:10, and this proportion can be used to estimate the amount of Pb that would be released in the gastrointestinal system [78]. Less Pb was extracted from samples in Corcona, 31±20% (n=49), than in Tornamesa, 45±38% (n=31), and in the car wash locations, 52±11% (n=9) ($p<0.05$) (Figure 2.6). A subset of 10 samples from these towns was also analyzed previously [78] by the standard bioaccessibility (IVBA) method from Drexler and Brattin [46] which extracted 60±31% of the total soil Pb (n=10). Additional correlation analysis of a suite of elements analyzed by XRF the soil samples (Figure B.8) further show geochemical differences between towns.that could explain these differences. Comparison of Pb in different particle sizes, fine (<250 μm), large (>250 μm), and total (Figure B.9), however, does not indicate a clear difference in the ratio of Pb in the fine fraction between towns. Concentrations of Pb in the smaller grain size (<250 μm) are not significantly higher than Pb concentrations in total sample, while the larger grain

size (>250 μm) particles contain about half of the Pb concentrations in the total sample (Figure B.9).

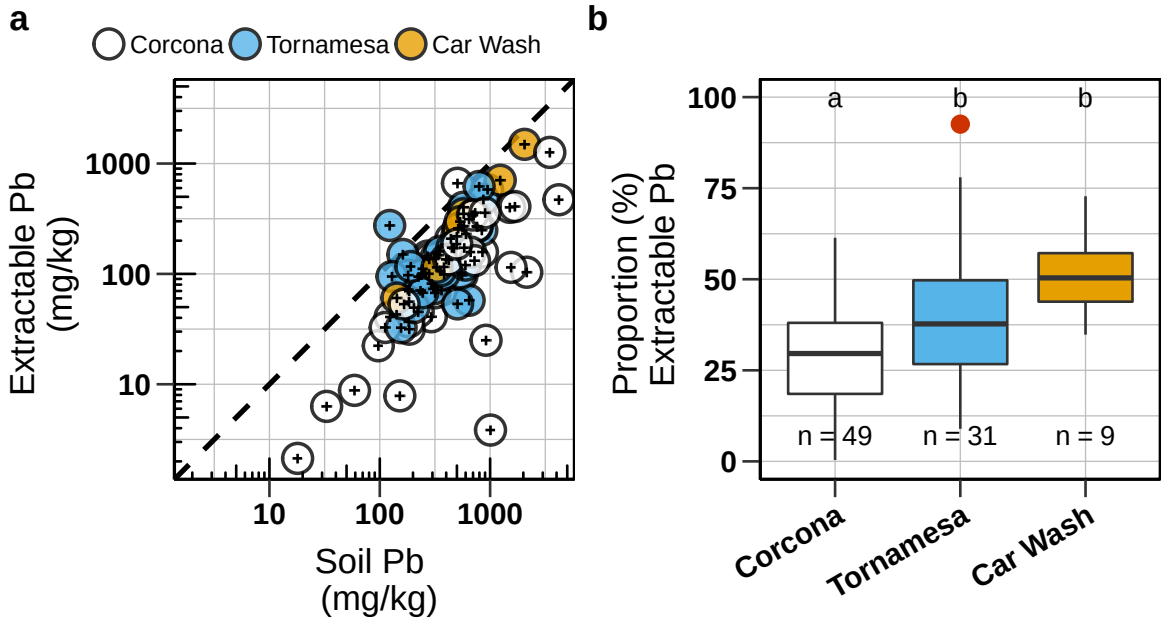

Figure 2.6: (a) Extractable Pb compared to total soil Pb from samples parents collected in areas where their children play and could play, by town. Concentrations were measured by XRF for total Pb in soil and by ICP-MS for extractable Pb. Error bars are 10%. (b) Proportion of extractable Pb is higher in Tornamesa and car wash areas than in Corcona. Two outliers that extracted more than 100%, after accounting for the dilution of 1g soil in 10 mL extraction solution, are outside the boundaries of plot b. Different letters in (b) represent groups that are statistically different ($p<0.05$).

2.5.6 Parent feedback

Parent feedback on using the field procedure revealed that parents found the procedure fairly easy to use (mean: 7.3±1.9, ±1 SD, on a scale from 1 for very difficult to 9 for very easy). Parents were also fairly confident (mean: 3.6±0.9 on a scale from 1 for not at all confident to 5 for very confident) that they could correctly gauge the color of the field-procedure test strip and that they could collect the soil sample and add it to the extract solution (mean: 3.2±0.9 on 1-5 scale). Parents reported some confidence in being able to do the entire procedure independently (mean: 3.0±1.1 on 1-5 scale). When asked who they thought should collect the soil samples, parents selected, in decreasing order, themselves (n=9), CREEH researchers (n=4), the government (n=4), a specialist for soil samples (n=3), and the health department

(n=1). However, most parents stated that they preferred the field-procedure color analysis be conducted by CREEH researchers (n=9), followed by themselves (n=6), a soil-sampling specialist (n=4), and the government (n=2).

2.5.7 Home soil samples

For home samples confirmed to have been collected indoors, the mean Pb concentration is 210±130 mg/kg (n=54, range: 40-780 mg/kg Pb) during Survey 1 and 280±210 mg/kg (n=50, range: 30-1500 mg/kg Pb) during Survey 2 (mean±1SD). For those samples confirmed to have been collected outside of the home, mean Pb is 270±200 mg/kg (n=49, range: 40-1080 mg/kg Pb) during Survey 1 and 280±170 mg/kg (n=68, 50-900 mg/kg Pb) during Survey 2.

Across all home samples, samples collected during Survey 1 correlate with samples collected during Survey 2 (Spearman's r_s=0.34, p<0.001). However, when looking at only the 24 samples collected indoors during both surveys, the correlation is higher (Spearman's r_s=0.58, p=0.004), which markedly improves when removing one outlier (Spearman's r_s=0.77 p<0.001) (Figure 2.7a). Concentrations of Pb for soils collected outdoors during both surveys do not correlate significantly (Spearman's r_s=0.31, p=0.079) (Figure 2.7b).

Home soil samples in relation to the broader environment

Average Pb concentrations (mg/kg Pb±1SEM) in outdoor home soil samples are, in towns with a hotspot, Corcona and Tornamesa (310±40, n=29 and 350±10, n=2), and in towns without a hotspot, Cocachacra and Carachacra (210±30, n=17 and 130, n=1). In indoor home samples average Pb concentrations in Corcona and Tornamesa (200±20, n=23 and 190±30, n=10) are similar to Cocachacra and Carachacra (230±40, n=18, n=17 and 290±100, n=3).

To assess the impact of local soil-Pb variation on home soil-Pb concentrations, we compared mean neighborhood soil-Pb, calculated from the 5-9 measurements taken within 100

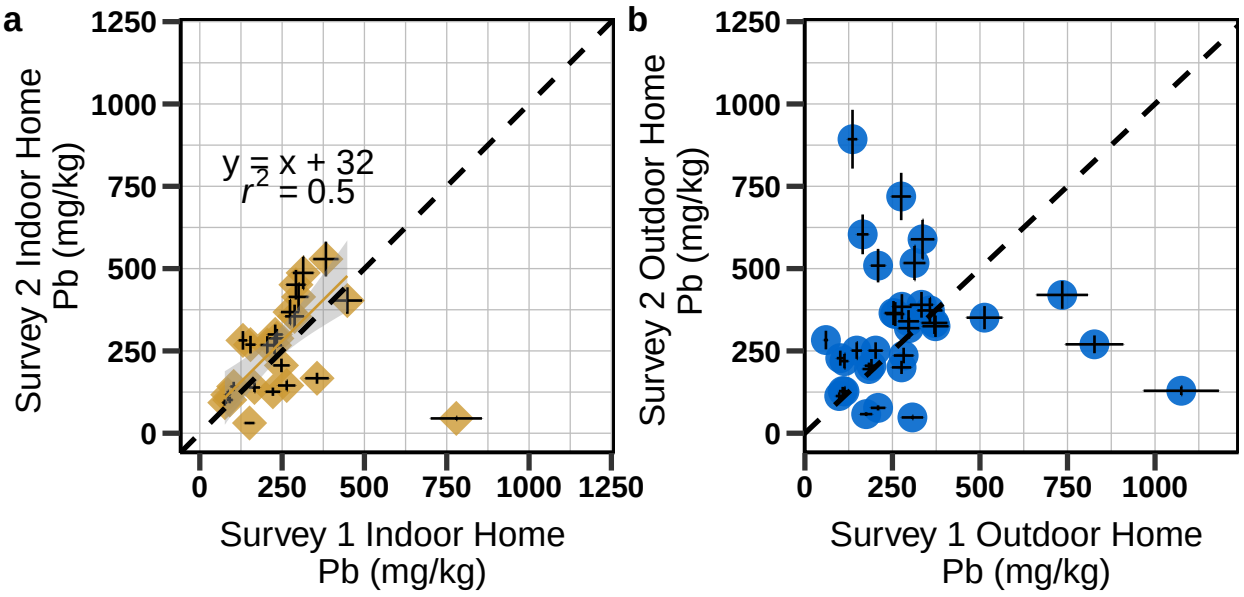

Figure 2.7: Lead concentrations in (a) indoor and (b) outdoor home samples measured by XRF in dust or soil collected during Survey 1 (July) and the Survey 2 (September). Many people swept and mopped daily and did not have enough dust inside the home for an indoor sample. Error bars are 10%. Best-fit line calculated without the outlier.

m of the homes in the 2015 roadside XRF mapping, to indoor and outdoor home samples from Survey 1 (Figure B.3). There is a significant correlation of the 47 confirmed outdoor home samples paired with neighborhood soil data (Spearman's r_s=0.43, p=0.003, n=47). However, this is not the case for indoor samples paired with neighborhood soil data (rho=-0.04, p=0.786, n=49). By town, average Pb concentrations (mg/kg Pb±1SEM) within 100 m of a home are higher in the towns with a hotspot, Corcona and Tornamesa (430±40, n=64 and 370±30, n=18), than in towns without a hotspot, Cocachacra and Carachacra (180±10, n=45 and 190±10, n=13, $p < 0.05$). Including the 2016 soil-Pb data increases the average in Corcona and Tornamesa (590±60, n=65 and 400±40, n=20), but does not change the correlation between 100 m soil-Pb and home soil-Pb samples.

2.5.8 Associations between blood and soil-Pb

There is no correlation between an individual child's BLL and Pb concentrations in home soil samples, whether confirmed indoor samples (Spearman's r_s: 0.02, p=0.887, n=50) or outdoor

samples (Spearman's r_s: -0.04, p=0.786, n=50) (Figure 2.8). There is also no correlation between BLL and mean Pb of the 2015 soil samples collected within 100 m of the home (Spearman's r_s: -0.03, p=0.734, n=135). This does not change when including soil-Pb data from the 2016 follow-up in the mean Pb concentrations within 100 m (Spearman's r_s: 0.06, p=0.520, n=138). Soil-Pb concentrations are not significantly associated with categorical BLL of the youngest child (Table 2.2).

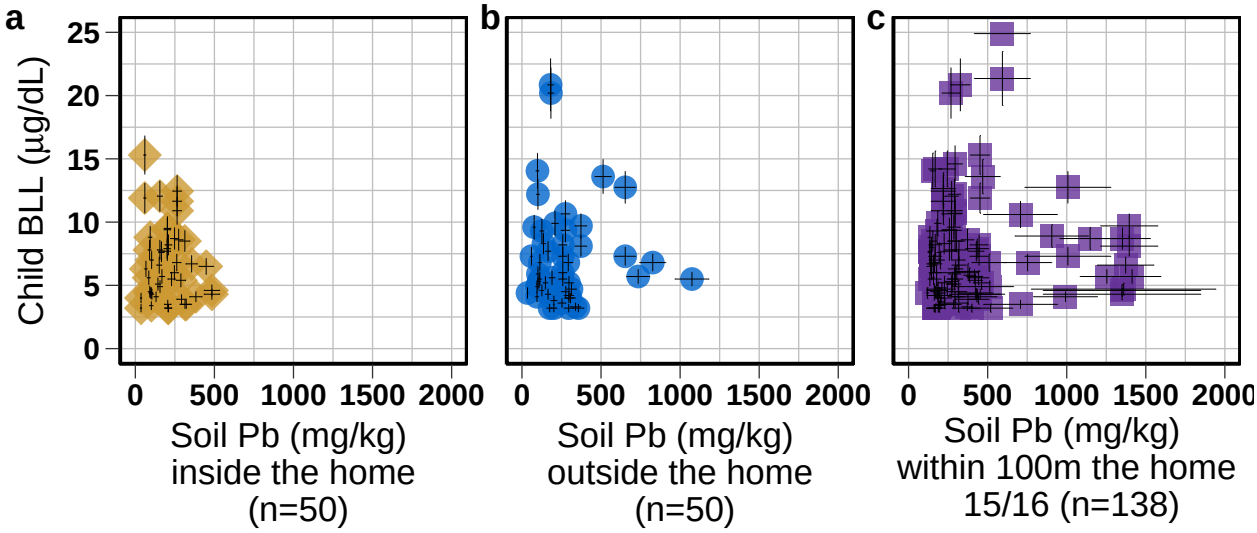

Figure 2.8: Child blood lead levels (BLL) with Pb levels from (a) soil or dust collected inside the home, (b) soil collected just outside the home, and (c) the average of soil samples within 100m of the home measured by roadside XRF mapping. All child BLL shown: if a parent had more than one child, then the parent's soil samples are repeated. Pb concentrations measured by XRF. Error bars are 10% for soil Pb inside and outside of the home. For soil Pb within 100m of the home, error bars are the standard error of all the soil measurements averaged.

Similarly, there is no correlation between child BLL and Pb in soil samples collected by the parent in areas where the child currently played (Spearman's r_s: -0.01, p=0.953, n=29) (Figure B.4a). If examined by category of BLL, the distribution of Pb concentrations in the soil samples collected by parents do not differ noticeably between the families with child BLL categorized as low (<5 µg/dL), medium (5-10 µg/dL) or high (>10 µg/dL) (Table 2.2, and Figure B.5a). The differences are larger when comparing the extractable Pb to these BLL categories, especially the absence of a highly extractable Pb in the lowest BLL category of

<5 µg/dL (Figure B.5). However, BLL is not correlated with the extractable Pb measured by ICP-MS either (Spearman's r_s: 0.13, p=0.512, n=29) (Figure B.4b).

2.5.9 Associations between blood and interview information

Blood-Pb levels for all children show significant associations with two observations recorded by the interviewer during Survey 1, before any child BLL information had been obtained (Figure 2.9, Table 2.2). Interviewers recorded whether the parents' clothing and shoes appeared dirty on a scale from 1 (not at all) to 4 (very much); the highest recorded value was 3 (very). Both observations of the cleanliness of parents' shoes (Spearman's r_s: 0.29, p=<0.001, n=138) and clothing (Spearman's r_s: 0.31, p=<0.001, n=136) are significantly correlated and associated with categorical child BLL groups (p=0.035 and p=0.005; Table 2.2). Finally, the proportion of children observed playing on the ground neared significance across categorical child BLL groups (p=0.053) and correlation (Spearman's r_s: 0.16, p=0.067, n=138).

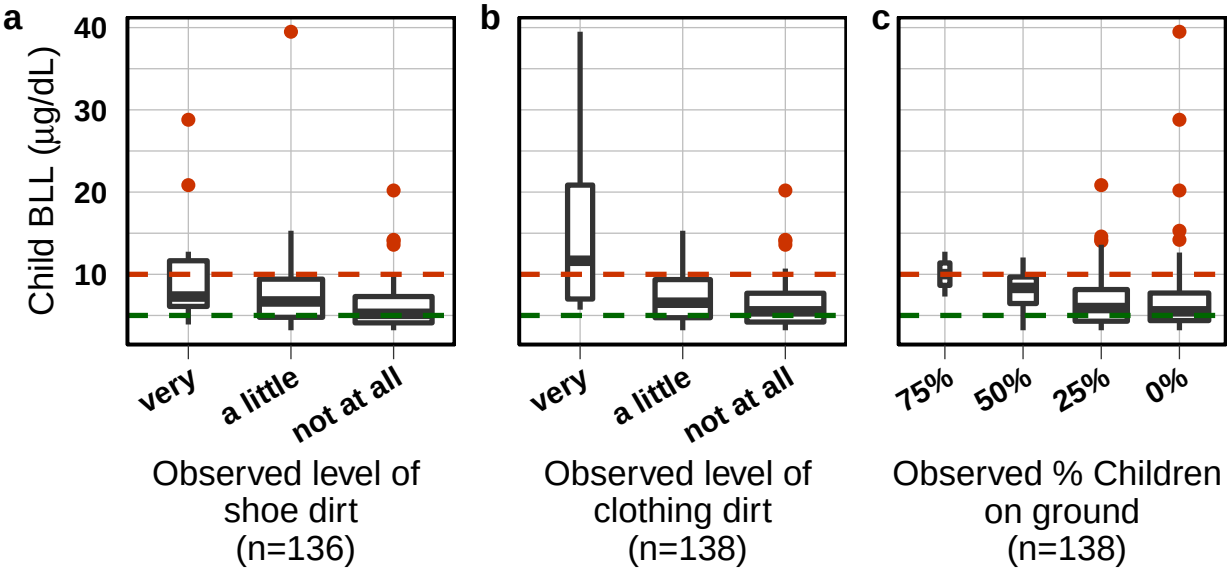

Figure 2.9: Child BLL by (a) observed level of shoe dirt, (b) observed level of clothing dirt, and (c) observed percent of children playing on the ground. All child BLL shown: if a parent had more than one child, then the parent's soil samples are repeated.

Child age, which is often associated with BLL, is not significantly correlated (spearman's rho: -0.03, p=0.756, n=143) when looking at each child individually (Figure B.6). However, parent education level is correlated with BLL when looking at each child individually, thus repeating parent education levels for parents with more than one participating child (Spearman's r_s: -0.19, p=0.029, n=138) (Figure B.7). This association is just not significant when looking at only the youngest child of each parent (Spearman's r_s: -0.15, p=0.107, n=110) and not at all across BLL category (p=0.472, Table 2.2). Neither of these interpretations change when removing the outlier of the child BLL near 40 μg/dL. Other factors such as self-reported behaviors avoiding contaminated areas, washing hands, or removing shoes when arriving at home were not associated with child BLL (Table 2.2). Child BLL was also not associated with type of water pipes used, purchasing informal gasoline, using artisanal paints, using traditional medicines, a parent working in mining, extended family working in mining, a family member recycling batteries or electronic waste, income, or size of home (Table 2.2). In some cases answers were practically uniform across all participants; for instance only one home reported having metal pipes.

For these analyses, results from Survey 1 are used because meeting attendance was low across all towns; only 14 of the 68 community meeting attendees were parents in the study. In total, only 10% of study participants attended the community meeting. However, 70% reported seeing at least one poster with the map of Pb contamination and 44% reported seeing the map at least once a day (Table 2.2). Parents ranked the map as easy to understand, on a scale from 1 (very difficult) to 5 (very easy), with an average of 4.1±0.9. When asked why they did not attend the meeting, 59% said they didn't know about the meeting, and another 7% said they didn't have enough information about the exact time and location of the meeting. Other common reasons included being unavailable due to work (10%), family obligations (7%), and other activities (12%).

2.6 Discussion

2.6.1 Causes and variations of Pb contamination

Pb concentrations in soil in these four mining-impacted towns vary greatly and, importantly, high levels of contamination are concentrated in hotpots, confirmed by XRF as soil >1,200 mg/kg Pb. The Corcona hotspot extended from the gates of a mining school situated on a former mine that produced barite, galena, and sphalerite, and along the levee protecting Corcona from the nearby River Rimac. The levee was reportedly constructed in part with waste material from the nearby mine. The Tornamesa hotspot was centered around the railroad turntable. However, we did not find the expected hotspots along the rest of railroad running through the four towns, even though uncovered flatbed railroad cars historically passed through carrying ore concentrate from the La Oroya smelter and mining areas. Replacement of railroad ties, which we observed happening in Cocachacra, likely covered past contamination along other sections. The railroad section in Tornamesa may remain contaminated because train cars spend more time above these track sections as they are uncoupled and recoupled around the turntable.

Parents collecting soil samples in 2016 from areas where their children play and screening samples using a field procedure identified a new hotspot of Pb contamination that we had missed in our 2015 mapping. While we had stayed on publicly accessible paths and roads, these new highly contaminated samples came from and around the excavated sites of new home construction. The excavation likely brought up underlying mine tailings that had been capped with low-Pb surface soil. It is unclear whether we missed this hotspot in 2015 due to staying on public-access ways or because there was less construction. These areas were not fenced off and we observed children playing in them.

Since the hotspots may represent different types of Pb contamination, it is not surprising to see variations in extractable Pb (Figure 2.6), which can be used to calculate bioaccessible Pb, or the proportion absorbed by the gastrointestinal system. Bioaccessibility of Pb depends

on its chemical form, size fraction, and the soil matrix [45, 49]. Lead from mining sources is often less bioaccessible than Pb from leaded-gasoline, smelters, or urban areas [45, 49, 78, 87]. The lead contamination in Corcona is likely from the nearby mine, and probably for that reason less extractable. Lead found in Tornamesa along the railroad turntable is from the ore concentrate carried by the trains, and thus more processed and extractable. Correlation analysis (Figure B.8) further confirm these geochemical differences between the soil samples between towns that could be relative to the different forms of contamination. The difference in extractability is not due to differences in Pb in the fine particle size, as no clear difference is seen between Corcona and Tornamesa (Figure B.9). Reassuringly, the Pb concentrations in the total soil sample (<1 mm) appear to be representative of particles more likely to stick to hands and clothes: concentrations of Pb in the smaller grain size (<250 μm) are only slightly higher than Pb concentrations in the total sample.

2.6.2 Child BLLs in relation to previous observations

Geometric mean BLLs in children under 6 years of age in the four towns (6.4 μg/dL) were markedly higher than BLLs in U.S. children (0.84 μg/dL in 2013-2014) [15]. In 65% of 200 children, BLLs were above the CDC reference value of 5 μg/dL while only 0.5% of U.S. children were over this value in 2013-2014 [15]. On average BLLs in 15% of children were over 10 μg/dL, although Tornamesa stands out with almost twice as high a proportion (32%, n=28). These proportions, however, are lower than most of the previously reported Peru BLLs above 10 μg/dL, including 58% of 335 children in La Oroya [71] and 53% of 356 children in Cerro de Pasco in 2008 [76]. Subsequent studies in Cerro de Pasco show a decrease from 2012, when BLLs for 44% of 2,671 children exceeded 10 μg/dL [88], to 2014 when only 17% of 757 children exceeded this level [89]. Compared to our study towns, both Cerro de Pasco and La Oroya are larger industrial cities with a history of Pb contamination and exposure from open-pit mining and ore smelting, respectively.

Geometric mean (GM) BLL in Corcona (6.4 μg/dL), Tornamesa (7.2 μg/dL), Cocachacra

(6.8 μg/dL), and Carachacra (5.6 μg/dL) were comparable to those reported in Cartagena, Colombia (4.7 μg/dL, n=189 school children age 6.9±0.1) in 2004 [90], as well as the 6.8 μg/dL found in Mexico in 1,207 adolescents (age 1-14) and the 4.9 μg/dL found in 2,001 infants (< 1 year of age) since 2000 [22]. At the other end of the spectrum, BLLs in these Peruvian towns were far below the ones measured in the Mitrovica region in the United Nations Administered Province of Kosovo between 1999 and 2007, where geometric mean BLL of 98 children was 50.3 μg/dL in 1999-2004 and dropped to 25.6 μg/dL for 16 children tested in 2006-2007 [91].

2.6.3 Environmental factors impacting BLL

Somewhat to our surprise, we do not see a correlation between BLL and soil-Pb or dust-Pb concentrations, whether within 100 m of the home (p=0.734), in outdoor home samples (p=0.786), or in indoor home samples (p=0.887). Similarly, we do not see a correlation between BLL and mean soil Pb in samples collected by parents where their children played. Our sample size is limited however, and while association between soil Pb and BLL is difficult to measure [26], it has been reported elsewhere [29, 30, 52, 76]. In addition, Lanphear et al (1998) found home dust-Pb loadings to be the major contributor to child BLL (Lanphear et al., 1998) and had previously found that dust-Pb loading were much more associated with child BLL than dust-Pb concentrations alone [5,28]. Dust-Pb loading data, e.g. Pb per area, was not collected in this study, and the indoor home soil samples sieved to <1mm and may not reflect exposure to Pb from dust as well as wipe samples, vacuum samples, or samples sieved to <250 or <150 μm, the fraction that sticks to children's hands. Homes that were too clean and did not have a sufficient amount of dust to be collected for analysis by XRF, do not have indoor home data, thus biasing the data set.

The association between BLL and total soil-Pb concentrations could be obscured by variations in the bioaccessibility of Pb, which are different between the towns and their contamination sources. Based on this, it was expected that extractable-Pb concentrations

in samples collected by parents where their children played, might better reflect child BLL. However, while there were no samples with high extractable Pb in the lowest BLL category below 5 μg/dL (Figure B.5), extractable Pb did not correlate significantly (r_s: 0.13, p=0.512, n=29) with BLL (Figure B.4b, Table 2.2), potentially due to the small sample size. Comparing aggregate community BLL to soil Pb supports the difference in bioaccessible Pb, or other factors varying impacting child BLL at a community level. For example, in Tornamesa the mean soil Pb is 680 mg/kg and BLLs in 32% of children >10 μg/dL (GM BLL 7.2 μg/dL), whereas in Corcona the mean soil Pb is higher, at 760 mg/kg, and BLLs >10 μg/dL for only 13% of children (GM BLL of 6.4 μg/dL) (Figures 2.3 and 2.4).

Past studies have found that dust lead concentrations and loading rates were difficult to accurately measure and reflected the myriad of socio-economic and behavioral factors [26,52]. Samples collected at a single point in time may not accurately reflect the average conditions a child is exposed to because of spatial and temporal variability of Pb in soil. This is indicated, for instance, by the lack of correlation of soil Pb outside the home between Survey 1 and 2 (Figure 2.7). And while soil Pb within 100 m is correlated (r_s=0.43, p=0.003, n=47) with outdoor home Pb, the relationship is far from consistent (Figure B.3). This suggests that soil-Pb is so variable that sampling does not properly represent soil-Pb concentrations that children are exposed to. Furthermore, since data on how much time a child spends where is not available, the soil we tested around a child's home may not represent the Pb levels to which a child is most exposed. When parents collected soil samples where their children played, at least two (of twenty) traveled more than 1 km to collect samples, in one case from a grandparent's home in the neighboring town. Some children attend school in different towns while young children may spend most of the day with their parent at work: in one case soil-Pb concentrations near a car wash area were up to 3,000 mg/kg. Cars and trucks coming down from the mountain potentially include mining-related vehicles covered with Pb-contaminated dust.

Children are potentially exposed to Pb from a variety of sources, and soil Pb or home

dust-Pb may not be the primary drivers of child BLL in this region. Drinking water is, however, likely not a contributing factor as water analysis from the public drinking water sources and supply all samples contain <1 μg/L Pb, and all but one home had plastic pipes. We did observe a local parent collecting water from the stream in Tornamesa that contained up to 3 μg/L Pb (unfiltered), who clarified that while she knew this was not drinking water, she would consider it safe to drink after boiling. In these towns, child BLL was also not associated with parent survey responses about the use of informal gasoline, artisanal paints, or traditional medicines, or a parent or family member working in mining, battery recycling, or electronic waste (Table 2.2).

Because the proportion of elevated child BLL varies by both soil and dust Pb levels, we ran multiple scenarios of the Integrated Exposure Uptake Biokinetic Model (IEUBK) for Lead in Children, varying input soil-Pb concentrations but keeping all other default values consistent. This model was used to determine the U.S. EPA hazard level of 400 mg/kg and 1,200 mg/kg and estimates that at soil-Pb concentrations less than or equal to 500 mg/kg, the probability that a single child's BLL would be greater than 10 μg/dL is 1 to 5% depending on dust-Pb concentrations [39]. The IEUBK model outputs estimates that BLLs in 0.4% of children ages one to six exceed 10 μg/dL when soil Pb is 200 mg/kg, and 28% exceed this level when soil Pb is 760 mg/kg. While this model is not inconsistent with our findings for Tornamesa, (mean soil Pb: 680 mg/kg, 32% >10 μg/dL), it overestimates the number of children who would exceed 10 μg/dL in the other towns of Corcona (soil Pb: 760 mg/kg, 13% >10 μg/dL), Cocachacra (soil Pb: 240 mg/kg, 13% >10 μg/dL), and Carachacra (soil Pb: 200 mg/kg, 0% >10 μg/dL).

Local conditions could be different from the basic assumptions of the IEUBK model, including that children spend more time outside in these Peruvian towns compared to the US, that some homes had dirt floors, and that low soil moisture conditions could increase soil resuspension. We therefore tested the sensitivity of the IEUBK model to varying the soil-ingestion rate to see if this could account for the difference in predicted and measured

child BLLs. Increasing the soil and dust intake rate 50% from the default raises the GM BLL from 2.9 to 3.8 μg/dL for children exposed to soil Pb of 200 mg/kg and from 7.6 to 10.4 μg/dL for children exposed to soil at 760 mg/kg Pb. These ingestion rate settings applied with town mean soil-Pb and home soil-Pb concentrations, result in the following BLLs: Carachacra (predicted 5.1 vs. measured 5.6 μg/dL), Tornamesa (7.4 vs. 7.2 μg/dL), Corcona (8.0 vs. 7.2 μg/dL), and Cocachacra (4.8 vs. 6.8 μg/dL). These variations indicate that there could be differing factors impacting BLL even between our study towns, such as the bioaccessibility of Pb in soil.

2.6.4 Parent and behavioral factors impacting BLL

Socio-economic and behavioral factors are well known to impact child BLLs [16, 92, 93]. Individual behaviors can impact the child BLL by interrupting the exposure pathway, and indeed in this study child BLLs were most significantly associated and correlated with the cleanliness of the parents' shoes ($p<0.001$) and their clothing ($p<0.001$). This indicates the importance of parents' behavior in the transfer of soil and dust Pb to children. While these observations could reflect interviewer bias, neither the participant nor the interviewer had knowledge of child BLL at this time. These factors are robust enough that they remain significant when considering only the youngest child per parent across BLL category (Table 2.2). While parent cleanliness is associated with child BLL, self-reported changing of clothing and shoes after coming home from work is not, nor is the appearance of the dustiness of the home (Table 2.2). It appears that the interviewer observations, rather than self-reported actions, better capture behaviors that are associated with child BLL, and perhaps represent more standardized or less biased indicators of behavior. The 2008 CDC report from Cerro de Pasco showed that increased BLLs were significantly associated with demographic factors such as child age and having a family member who worked in mining [76]. In our study the only demographic factor that significantly correlates with child BLL is parent education level ($p=0.029$) when looking at all children, repeating parent education levels in the case

of multiple children from the same parent. Parent income, number of rooms in a home, and child age are not significantly associated. However, even parent education level is not significantly correlated when looking at only the youngest child of each parent (p=0.107) or across BLL category (p=0.472; Table 2.2). This could reflect the small sample size of n=110 when taking the youngest child per parent and n=138 when taking each child individually and repeating parental factors. Finally, child age and individual variations in child nutritional status, especially iron-deficiency, can also impact BLL [94]; nutritional information is not available for this study.

2.6.5 Limitations and challenges

The outcome of this study is consistent with the limitations highlighted by the review by Laidlaw and Filippelli (2008) for determining the association between soil Pb and blood Pb, including misclassification of exposure due to limited point samples and low sample size [26]. While our study started out with a reasonable sample size, the number of paired child BLL data with Pb concentrations from indoor soil, outdoor soil, and play areas is very limited, especially across BLL category. In addition, not all factors that can impact child exposure to Pb, including spatial and temporal variations in total and extractable Pb in soil, indoor home soil and/or dust samples and size fraction, time children spend in which locations, child hand-to-mouth behavior, and child iron-deficiency, were adequately captured in this study.

2.6.6 Implications for parents collecting environmental data to reduce child Pb-exposure

A larger, more systematic intervention should be conducted to quantify the impact on child exposure of combining parent health education with parent-led environmental sampling and testing, given that (a) parent cleanliness was related to child BLL, (b) parents successfully

collected soil samples in this pilot study, (c) parents preferred they be the ones to collect soil samples, and (d) the high variation in total and extractable Pb concentrations in soil. There is considerable scope for testing the effectiveness of a more participatory approach, because educational interventions have been shown to reduce child BLL but are not always effective [95]. Covering, or replacing, high-Pb soil with clean soil has also been shown to reduce child BLLs [52, 53, 96]. Reducing indoor dust-Pb loading, has also been connected to decreases in child BLL, especially at higher BLLs [97, 98], although it appears there are diminishing returns at lower BLL [98].

For scaling up this approach, parents could collect soil samples where their children might be exposed and return these samples to a local health center or school, where trained staff analyze the samples with or for parents. In the case that such an intervention seeks to create community-wide maps of soil Pb, one challenge could be recording the geolocation of the samples with a touchscreen on a smartphone. In our study, younger parents or those accustomed to touchscreen phones had no difficulties, and we anticipate that this challenge would decrease with time as smartphones and touchscreens become more common in towns throughout the world.

2.7 Conclusion

The four small mining-impacted towns studied here contained hotspots of high concentrations of Pb in soil and children with elevated BLLs. Hundreds of similar towns exist in Peru and neighboring countries where children may be exposed but no environmental or exposure data are collected. This study shows that parents are motivated and capable of collecting soil samples using a simple field procedure to help identify these potential areas of hazardous soil Pb. Parents found an additional hotspot of Pb greater than 1,200 mg/kg that had not been identified by our original soil mapping. While there was no clear relationship between these parent-collected soil samples, or other soil samples, and child BLL, parent shoe and clothing

cleanliness was related to BLL and appears to link parents' behavior to the transfer of soil and dust Pb to children. Parent cleanliness may therefore be a valuable target of educational interventions, possibly as part of soil sampling and testing to identify and reduce exposure to hotspots of Pb contamination.

2.8 Acknowledgments

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Table 2.2: On the next pages: Child BLL categories with soil Pb and participant characteristics.

Table 2.2: Child BLL categories with soil Pb and participant characteristics

	BLL >10		BLL 5-10		BLL <5		ANOVA/Kruskal–Wallis test		
Soil Pb factors	**Mean (n)**	**Median (IQR 25%-75%)**	**Mean (n)**	**Median (IQR 25%-75%)**	**Mean (n)**	**Median (IQR 25%-75%)**	**p-value**		
Indoor House Pb (mg/kg)	215 (4)	210 (131-293)	207 (22)	203 (145-259)	209 (14)	181 (102-309)	*p=0.999*	nonnorm	kruskal.test
Outdoor House Pb	317 (6)	229 (182 - 454)	301 (18)	200 (119 - 296)	231 (12)	265 (153-309)	*p=0.886*	nonnorm	kruskal.test
Soil Pb 100m	385 (16)	283 (239-456)	417 (51)	297 (173-431)	419 (39)	285 (191-433)	*p=0.889*	nonnorm	kruskal.test
Soil Pb 200m	420 (17)	341(197-448)	500 (51)	361 (282-727)	416 (3)	337 (197-420)	*p=0.41*	nonnorm	kruskal.test
Soil Pb 100m - 2015 only	345 (14)	273 (220 -333)	287 (51)	286 (173-345)	394 (39)	263 (191-368)	*p=0.73*	nonnorm	kruskal.test
Soil Pb 200m - 2015 only	382 (15)	286 (197-380)	392 (51)	315 (259-377)	402 (39)	286 (197-410)	*p=0.785*	nonnorm	kruskal.test
Fieldkit soil Pb in areas where children play	413 (6)	377 (300-505)	728 (7)	528 (406-780)	560 (6)	518 (318-726)	*p=0.524*	nonnorm	kruskal.test
Fieldkit extractable Pb in areas where children play	185 (6)	140 (125 - 224)	253 (7)	216 (116-284)	140 (6)	129 (89 - 198)	*p=0.524*	nonnorm	kruskal.test
Fieldkit total soil Pb all samples	625 (6)	558 (386-829)	684 (7)	523 (423-744)	474 (6)	433 (296 - 619)	*p=0.572*	nonnorm	kruskal.test
Fieldkit extractable Pb in all areas	237 (6)	155 (123-282)	234 (7)	216 (126-265)	126 (6)	131 (90 - 173)	*p=0.324*	nonnorm	kruskal.test
	BLL >10		**BLL 5-10**		**BLL <5**				
Observational	**n (%)**		**n (%)**		**n (%)**		p-value		
How dusty was home							*p=0.854*	chi-square test	
Not at all	2 (15)		12 (22)		10 (29)				
A little	7 (54)		30 (56)		18 (51)				
Very	4 (31)		12 (22)		7 (20)				
Shoes dirty							**p=0.035**	chi-square test	
Not at all	4 (25)		28 (53)		25 (68)				
A little	8 (50)		18 (34)		11 (30)				
Very	4 (25)		7 (13)		1 (3)				
Clothing dirty							**p=0.005**	chi-square test	
Not at all	5 (31)		35 (65)		27 (73)				
A little	7 (44)		16 (30)		10 (27)				
Very	4 (25)		3 (6)		0 (0)				
How many children <6 playing on the ground							**p=0.053**	chi-square test	
None	7 (44)		24 (44)		23 (62)				
25%	5 (31)		26 (48)		13 (35)				
50%	3 (19)		4 (7)		1 (3)				
75%	1 (6)		0 (0)		0 (0)				
participant observed child							*p=0.368*	chi-square test	
Not at all	3 (19)		18 (33)		15 (42)				
A little	4 (25)		16 (30)		11 (31)				
Very	9 (56)		20 (37)		10 (28)				
observed shoes removed							*p=0.801*	chi-square test	
None	16		53		36				
25%	0 (0%)		1 (2%)		1 (3%)				
observed clothes changed							*p=0.368*	chi-square test	
None	16		52		37				
25%	0 (0%)		2 (4%)		0 (0%)				

Table 2.2 (continued): Child BLL categories with soil Pb and participant characteristics

	BLL >10		BLL 5-10		BLL <5		ANOVA/Kruskal–Wallis test		
Other factors	**Mean (n)**	**Median (IQR 25%-75%)**	**Mean (n)**	**Median (IQR 25%-75%)**	**Mean (n)**	**Median (IQR 25%-75%)**			
Spending time in likely contaminated areas	2.1 (14)	2.1 (1.0-3.0)	1.8 (51)	1.6 (1.0-2.5)	1.7 (36)	1.4 (1.0-2.2)	*p=0.45*	nonnorm	kruskal.test
Avoiding likely contaminated areas	1.5 (14)	1.0 (0.5-2.5)	1.9 (51)	2.0 (1.0-2.5)	2.0 (36)	2.0 (1.0-3.0)	*p=0.38*	nonnorm	kruskal.test
Picking up the child in likley contaminated areas	2.6 (14)	2.3 (1.3-4.0)	2.3 (51)	2.0 (1.0-3.3)	2.2 (36)	1.8 (1.0 - 3.5)	*p=0584*	nonnorm	kruskal.test
Child sucking thumb	2.8 (16)	2.5 (1.9-4.0)	3.0 (54)	3.0 (2.0-4.0)	3.0 (37)	3.0 (2.5-4.0)	*p=0.799*	nonnorm	kruskal.test
Child wash hands before eating and after playing outside	3.1 (16)	3.7 (2.6-4.0)	3.2 (54)	3.3 (2.7-4.0)	3.3 (37)	3.7 (2.7-4.0)	*p=0.896*	nonnorm	kruskal.test
Removing shoes when coming home (1=almost never, 5 = almost always)	1.3 (16)	1.0 (1.0 - 1.0)	1.7 (54)	1.0 (1.0-2.0)	1.5 (37)	1.0 (1.0-2.0)	*p=0.2*	nonnorm	kruskal.test
Change clothing when getting home from work	2.5 (16)	2.5 (1.0 - 3.1)	2.9 (54)	3.0 (2.0 - 4.0)	2.9 (37)	3.0 (1.0 - 4.0)	*p=0.512*	nonnorm	kruskal.test
	n (%)		**n (%)**		**n (%)**				
Saw a poster of soil Pb	10 (71)		35 (65)		26 (70)		*p=0.816*	chi-square test	
Live in town with hotspot	10 (63)		32 (59)		59.5% (37)		*p=0.972*	chi-square test	
Do you paint your home with "artesnal"paint?	2 (13)		7 (13)		1 (3)		*p=0.229*	chi-square test	
Do you buy informal gasoline?	3 (33)		2 (22)		0 (0)		*p=0.240*	chi-square test	
Do you have metal pipes?	0 (0)		1 (2)		0 (0)		*p=0.434*	chi-square test	
Do you use traditional medicines?	12 (75)		31 (57)		24 (65)		*p=0.416*	chi-square test	
Demographic factors	**n (%)**		**n (%)**		**n (%)**				
Gender (woman)	15 (94)		47 (87)		35 (95)		*p=0.429*	chi-square test	
Literacy (read and write)	15 (94)		52 (96)		36 (97)		*p=0.177*	chi-square test	
Secondary school or higher	12 (75)		44 (82)		33 (89)		*p=0.472*	chi-square test	
Participant or spouse works in mining	3 (19)		10 (19)		7 (19)		*p=0.750*	chi-square test	
Other family member works in mining	6 (38)		16 (30)		14 (38)		*p=0.674*	chi-square test	
Family member recycles batteries	0 (0)		4 (7)		3 (8)		*p=0.513*	chi-square test	
Family member recycles electronic waste	0 (0)		4 (7)		1 (3)		*p=0.365*	chi-square test	
	Mean (n)	**Median (IQR 25%-75%)**	**Mean (n)**	**Median (IQR 25%-75%)**	**Mean (n)**	**Median (IQR 25%-75%)**			
# Rooms in household	2.6 (16)	2 (1.8-4)	2.9 (54)	2 (2-3)	3.5 (37)	3 (2-5)	*p=0.139*	nonnorm	kruskal.test
How many m2 is house	95.6 (16)	85 (75-120)	94.5 (54)	90 (52.5 - 120)	102 (37)	90 (60-100)	*p=0.914*	nonnorm	kruskal.test
Age of parent	32 (16)	30 (27-38)	34 (54)	32 (27-39)	32 (37)	31 (24-38)	*p=0.525*	nonnorm	kruskal.test
Monthly expenses (PEN)*	612 (16)	550 (388-675)	628 (54)	600 (363-738)	576 (37)	600 (300-800)	*p=0.892*	nonnorm	kruskal.test
Monthly income (PEN)*	1069 (16)	1100 (775-1350)	1182 (54)	1000 (800-1500)	1142 (37)	1000 (750-1500)	*p=0.913*	nonnorm	kruskal.test
Age of youngest child	2.44 (16)	2.0 (2.0-3.0)	3.0 (54)	3.0 (2.0-4.0)	2.7 (37)	2.6 (0.9 - 4.0)	*p=0.272*	nonnorm	kruskal.test

* 1 Peruvian Nuevo Soles (PEN) = 0.322 USD

Chapter 3

Hazardous levels of lead in soil identified with a kit by students in high school science classes

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3.1 Abstract

The toxic effects of lead (Pb) are well established and linked to environmental sources that are typically very heterogeneously distributed. In order to prevent exposure, these environmental sources must therefore first be identified. Many countries, however, do not have programs to systematically test for Pb in potentially hazardous areas. Here we show that integrating a sample collection and analysis program into upper-level high school science courses is an effective way to generate environmental data for making first order decisions, such as where to focus follow-up with more detailed sampling. Students in three Peruvian towns used a field procedure to screen soil, which can be contaminated with Pb, around their schools and where children play. Subsequent X-ray fluorescence analysis of student-collected samples, conducted by a local non-profit, confirmed high concentrations of soil Pb in Cerro

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de Pasco (2100±2000 mg/kg Pb, mean±1SD) and Callao (460±280 mg/kg Pb), and low concentrations in Ate (130±110 mg/kg Pb). Students gained a hands-on activity in their science class to collect data relevant to their families and their communities. Extending similar activities in classrooms around the world could thus be an effective way to generate not only relevant environmental data required to identify hotspots, but also to teach students about avoidable environmental health hazards and ways to reduce exposure.

3.2 Introduction

Globally, lead (Pb) exposure causes an estimated 1 million deaths and 24.4 million disability-adjusted life years (DALYs) each year [18], however these estimates do not capture the full health impact due to lack of information on exposure to soil pollution [17]. Furthermore, these harmful effects of Pb are not distributed evenly, with 82% of deaths due to Pb occurring in low- and middle-income countries (LMICs) [17]. For example, Peru is one of the top five countries for the production Pb and other polymetalic ores [99] and has an estimated 1.6 million people living within 5 km of an active or former mining operation [40]. Informal recycling of used Pb-acid batteries (ULAB) is another important source of Pb poisoning throughout LMICs. Only 50% of these batteries are recycled at authorized locations in Peru [100]. In the vast majority of potentially contaminated mining and industrial sites, there is no information about the distribution of Pb levels or the extent of Pb exposure.

Children are most at risk of Pb poisoning and can be exposed through incidental ingestion of contaminated soil, especially from fine dust and resuspended soil particles that stick to hands and toys [26, 29, 30, 32]. Elevated levels of soil Pb have been linked to child blood Pb levels (BLL) [28, 35, 52] and the toxic effects of Pb on the nervous and cardiovascular system are still being identified at lower BLLs [5, 8, 13]. Soil-Pb contamination is often spatially heterogeneous, a crucial fact that means once hotspots are identified they can be addressed

and uncontaminated areas are likely nearby.

This study describes how high school students successfully identified areas of hazardous Pb concentrations using a field procedure for soil Pb [78], thus generating and sharing the critical information of where young children should not play. The motivation is that incorporating environmental testing into high school classes can also serve to increase local knowledge about Pb and how to protect against these health hazards, as only 7% of the general population in Peru is aware of the health impacts of Pb [100]. In class, students first learn about the health risks of Pb and how to prevent exposure and then learn how to collect samples and analyze them using a field procedure. The field procedure uses a simulated gastric solution to extract soil Pb that is correlated to bioaccessible Pb [78]. In vitro bioaccessible methods determining how much Pb is released into solution and can thus be absorbed by the gastrointestinal system [46, 50] are more relevant to health risk than the total concentration of Pb in soil. This form of participatory citizen science was integrated as a hands-on project component in a Science and Technology high school course in three Peruvian cities with different types of Pb contamination: Ate, Callao, and Cerro de Pasco.

Ate is near a secondary Pb smelter site recycling batteries identified by CREEH and on the Pure Earth/Blacksmith Institute Toxic Site Identification Program (TSIP) [101, 102]. Soil Pb levels were found between 100 and 2000 mg/kg Pb and the operating battery recycler was determined to be the primary cause of elevated Pb in this residential area. While no exposure (e.g. BLL) data is available for the area, data from the TSIP program suggests that 6 to 16 million people globally are exposed to dangerous levels of Pb near ULAB recycling sites, for up to 1.6 million DALYs [103]. In Peru, all authorized Pb-acid battery recyclers are within densely populated areas of Lima and Callao, such as this one in Ate [100].

Callao is Peru's primary port for export just north of Lima and piles of mineral ore are waiting for transport in storage facilities in its Puerto Nuevo neighborhood. In 1999, a survey of 2,510 children under the age of 10 identified higher mean BLL (25.7 μg/dL) in the Puerto Nuevo neighborhood than the rest of Callao (9.9 μg/dL) or in the metropolitan

area of Lima (7.1 μg/dL) [73]. This survey led to follow-up studies to identify the exposure source that found elevated soil-Pb concentrations near the open mineral storage areas and connected the Pb isotope ratios in child blood samples to the ratios in the mineral ore, which were significantly different from those in gasoline [74]. A comparison of two schools near the mineral deposits to a school 5 km away in Callao found a decrease in child cognitive abilities with increase BLL [75].

Cerro de Pasco is home to an infamous open-pit mine primarily extracting Zn-Pb-Ag, with modern mining dating back to 1906 [104]. Reports of BLLs far exceeding the Peruvian reference level of 10 μg/dL began with a 2005 study by the Peruvian Ministry of Health finding that BLLs in 86% of 233 children exceeded 10 μg/dL [70] and a 2008 CDC report showing that BLLs in 50% of 356 children exceeded this level [76]. The CDC report also collected soil samples and found that soil samples from 79% of homes contained >400 mg/kg Pb, the U.S. Environmental Protection Agency hazard standard for bare soil where children play, and 60% were above 1,200 mg/kg. Of an additional 32 soil samples collected from public places, 84% exceeded 400 mg/kg and 66% exceeded 1,200 mg/kg. This study also found that increased BLLs were associated with higher soil-Pb levels, child age as well as whether children lived with someone who worked in mining, helped wash clothing, and were observed eating rocks or paint [76]. Conklin et al. recommended informing the community about the possibility of Pb contamination in public spaces and covering local soccer fields, which had a mean soil-Pb concentration of 1,500 mg/kg, with a clean layer of soil.

3.3 Materials and methods

3.3.1 Selection of sites

Schools were selected based on proximity to known sources of potential Pb contamination and based on interest from the principal and science teachers. Participating students were in their last two years of high school and signed assent forms; parents were informed of the

study during a parent meeting and provided their consent for their child's participation. All activities were integrated into their "Science and Technology" course, in conjunction and with the approval of the instructor. Participating classes included, in Ate four different class sections with a total of 91 students, in Callao one class of 16 students, and in Cerro de Pasco two classes for a total of 29 students.

All procedures involving students were approved by the Columbia Institutional Review Board and the Peruvian Comité de Ética de PRISMA (http://www.prisma.org.pe/comite-de-etica).

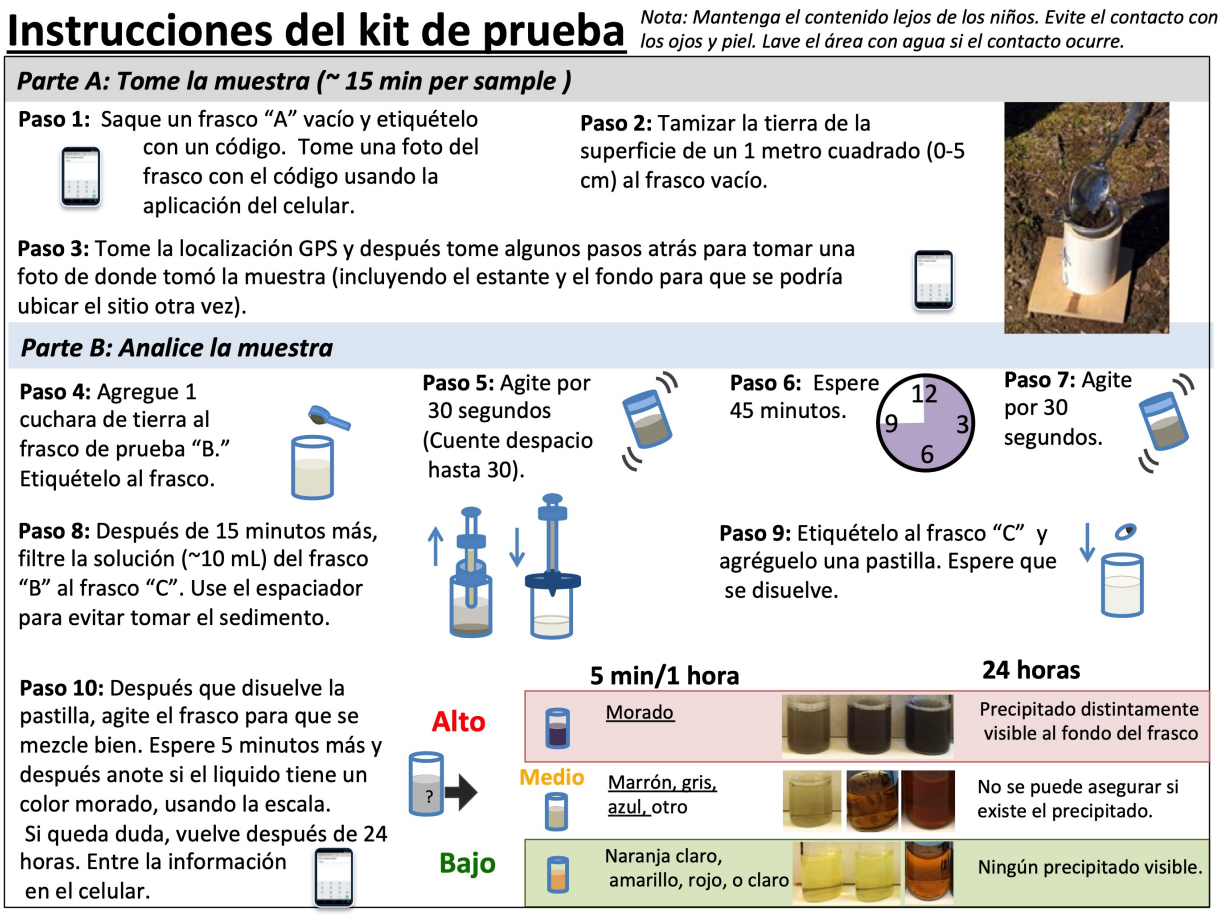

Figure 3.1: Steps of the field procedure to screen soil that students followed in their high school course, "Science and Technology". Figure is an updated version of the field procedure from [78].

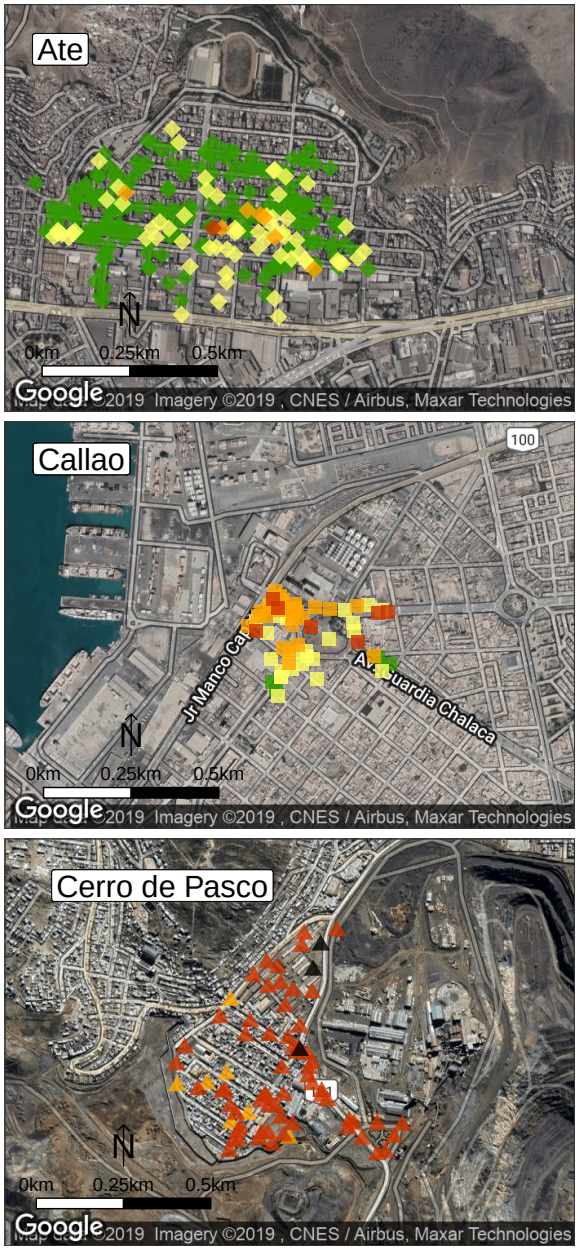

Figure 3.2: Soil-Pb concentrations measured by XRF in the three different towns in mg/kg: green (<140), yellow (140-400), orange (400-800), red (800-5,000) and black (>5,000).

3.3.2 In-class student activities

Class activities were divided into six Pb-themed sessions in the course. Students first (1) learned about environmental and Pb contamination, and in the second (2) class students discussed the health risks associated with Pb and how to protect themselves and especially younger siblings from Pb exposure. In the third (3) class, students learned why it was important to delineate where Pb contamination might be in their community and how and where to collect soil samples. In the fourth (4) class, students collected soil samples which they analyzed in the fifth (5) class with a field procedure outlined below (Figure 3.1). Students later combined their data with laboratory X-ray fluorescence data obtained independently in the sixth (6) class to create maps of their samples to share with their parents and communities in an extra after school session. A pre- and post-test survey was given to students before and after all class activities to assess their perceptions and knowledge about Pb contamination, as well as their interest and motivation in science.

3.3.3 Student soil sampling

Students, in groups of 3 to 5 to ensure sampling validity, collected soil samples approximately along a grid around the school on publicly accessible roads and parks (Figure 3.2). The instructor and additional trained research team members accompanied students in the field to ensure student safety and sampling integrity. Students were trained to use a stainless steel spoon to collect composite surface soil samples and sieve them through a 1 mm kitchen sieve directly into 20 mL plastic vials. Each individual soil sample was recorded by a unique sample ID with the SurveyCTO app [83] on a provided smartphone along with GPS coordinates, a photo of the sample site, and a brief description of the sample.

3.3.4 Soil analysis by the field procedure

Soil samples were analyzed in class using a field procedure to identify hazardous levels of Pb that combines a simulated gastric extraction with the color indicator sodium rhodizonate (Figure 3.1) [78]. The course instructor as well as CREEH research team members carefully supervised all procedures; safety precautions were followed and students wore gloves. In class, students added 1 scoop of approximately 1.5 g soil with a 1.5 mL scoop to 15 mL of a 0.4 M glycine solution with hydrochloric acid at a pH of 1.5. Soil mass in the 1.5 mL scoop averaged 1.9 ± 0.5 g (±1 standard deviation (SD), n=72). After an extraction time of 1 hour, students filtered the solution using a 0.45 μm syringe filter into a new clear vial and added a dissolvable capsule of 10 mg of sodium rhodizonate. A pH test strip was dipped into the vial in classes in Callao and Cerro de Pasco to confirm whether the solution remained acidic with a pH of 2 or lower; however, since the difference between pH 2 and 3 was difficult to determine on the test strip, all samples with a pH of 3 or lower were accepted. Once the color change occurred, students compared their vial to a color chart and ranked the sample "high" if the solution turned violet or extremely dark, "medium" if the solution turned brown or a darker color that was not violet, and "low" if the solution turned yellow, orange, red, or any light transparent color. Students recorded their observations, including a photo of the vial and the pH test strip, using again the smartphone-based SurveyCTO app [83].

3.3.5 Maps and presentation of soil-Pb results

Students received analytical results for the total Pb concentration in their soil samples analyzed by CREEH research staff using a handheld X-ray fluorescence instrument (XRF) as well as maps with the sample locations. Students colored the points based on the Pb concentration from the XRF as follows: green if Pb was below the 140 mg/kg Peruvian residential soil standard, yellow if Pb was 140 mg/kg or above but below the 800 mg/kg Peruvian industrial soil standard, and red if Pb was 800 mg/kg or above. Students worked with the instructor as well as CREEH staff to synthesize accurate information about Pb health risk.

Students then presented their soil-Pb maps to parents and interested community members at a local meeting in the school. Meetings were organized and supported by the school and CREEH, who also shared information on how to prevent exposure and what could be done at contaminated sites.

3.3.6 Additional analytical tests to confirm student results

Student assessment of the field procedure and color results were confirmed by additional testing by CREEH researchers. All samples were analyzed by XRF for Pb concentrations in the soil sample and in the field-procedure extract. Photos uploaded by students on SurveyCTO were reanalyzed for field-procedure color, pH test-strip reading, and any other visible sample description, blinded to the student-submitted rankings. Some photo-based rankings were limited by poor lighting conditions and out-of-focus images. A subset of 7 samples that had extracted more than 150% of the total amount of soil Pb was reanalyzed by the field procedure by CREEH researchers in Lima. An additional subset of 32 samples was reanalyzed by the field procedure at the Lamont-Doherty Earth Observatory, and the liquid extract was analyzed by inductively coupled mass spectrometry and a second X-ray fluorescence instrument.

3.3.7 Instrumental methods

X-ray fluorescence (XRF) analysis was conducted with a Thermo Scientific Niton XL3t portable XRF in Peru. Soil samples and extract solutions were analyzed for 90 seconds in the instrument's default soil mode. The reliability of the XRF measurements was confirmed by repeated analysis of reference materials (RM) RM 180-661 RCR1 with a concentration of 500 mg/kg Pb (mean measurement 90%, n=5), National Institute of Standards and Technology (NIST) 2709a with a published value of 17.3 mg/kg Pb (mean measurement 112%, n=2), and a blank SiO2 180-647 standard with <10 mg/kg Pb (mean measurement below the detection limit $<$ 3.8 mg/kg Pb, n=5). For XRF analysis of the extract solutions, Pb standards in

solution were prepared in the acidified glycine matrix and analyzed by XRF. All repeated analysis of a blank glycine solution resulted in Pb concentrations below the detection limit of 3.4 mg/kg (n=10). If liquid XRF measurements were below the detection limit, one-half the detection limit was retained for calculations and plots.

Concentrations of Pb in the subset of 32 samples reanalyzed were measured by XRF (Innov-X Systems DELTA Premium) for 60 seconds, with 20 seconds at each of the XRF's three incident-beam energies. For this XRF instrument, analysis was confirmed by measurements of NIST RM 2710 with 5,532 mg/kg Pb (mean 93% of the reference value, n=3), SRM 2711 with 1,162 mg/kg (105%, n=3), and SRM 2711a with 1,400 mg/kg (103%, n=4), and SRM 2709 with 18.9 mg/kg (190%, n=3). Although there is a discrepancy of the low Pb XRF readings, these were not adjusted. Liquid extracts were also analyzed by high-resolution (HR) inductively coupled plasma mass spectrometer (ICP-MS) (Thermo Scientific Element II). For ICP-MS analysis, data were accepted when concentrations of Pb obtained for NIST reference materials 1640A (mean recovery 100%, n=3) and 1643F (94%, n=3) were within 10% of their published values. All ICP-MS method and vial blanks contained <1 μg/L Pb.

3.3.8 Statistical analyses

Statistical analyses were performed with R Studio 1.2 ([84]) using R 3.5.1 ([85]) and packages). To check for significant differences between towns we employed a Kruskal-Wallis test for non-parametric continuous data and a Mann Whitney U test.

3.4 Results

3.4.1 Total-Pb concentrations in soil

Mean total soil-Pb concentrations varied greatly within and between the three towns: Ate (130±110 mg/kg Pb; mean±SD), Callao (460±280 mg/kg Pb), and Cerro de Pasco (2100±2000 mg/kg Pb) (Figures 3.2 and 3.3, $p<0.01$). Of the 276 soil samples collected in Ate around

the school, Pb concentrations in 74% of samples were <140 mg/kg, the Peruvian residential standard [81], and 97% were < 400 mg/kg, the U.S. Environmental Protection Agency soil hazard level for bare soil where children play [39]. In Callao, near the mineral storage deposits, Pb concentrations in only 8% of the 66 soil samples were <140 mg/kg and 47% were <400 mg/kg. However only 10% of samples exceeded 800 mg/kg Pb, the Peruvian industrial soil standard, and only 3% exceeded 1,200 mg/kg Pb, the U.S. EPA hazard standard for other soils. Soil-Pb levels in Cerro de Pasco were by far the highest; concentrations in all 73 samples exceeded 400 mg/kg, 90% exceeded 800 mg/kg, and 69% exceeded 1,200 mg/kg (Figure 3.3).

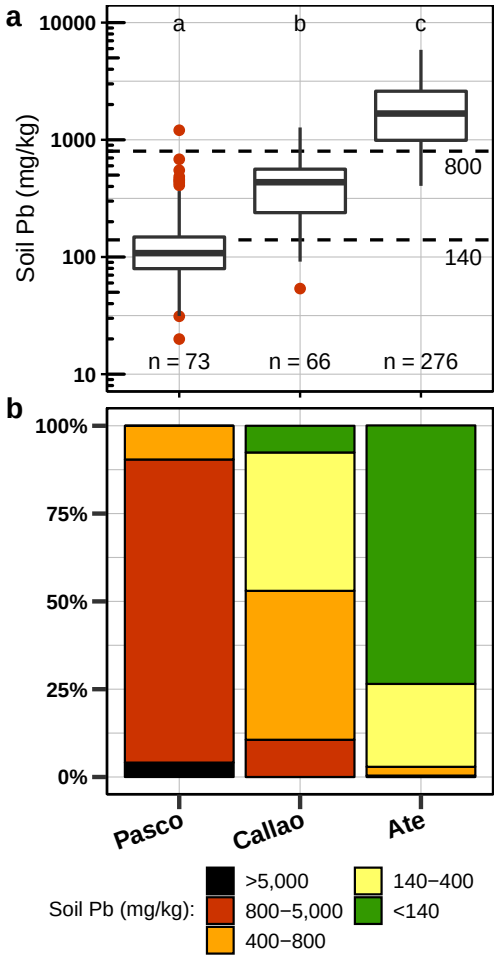

Figure 3.3: Distribution of total soil-Pb concentrations (mg/kg), measured by XRF, in Ate, Callao, and Cerro de Pasco. Different letters in (a) represent groups that are statistically different ($p<0.05$).

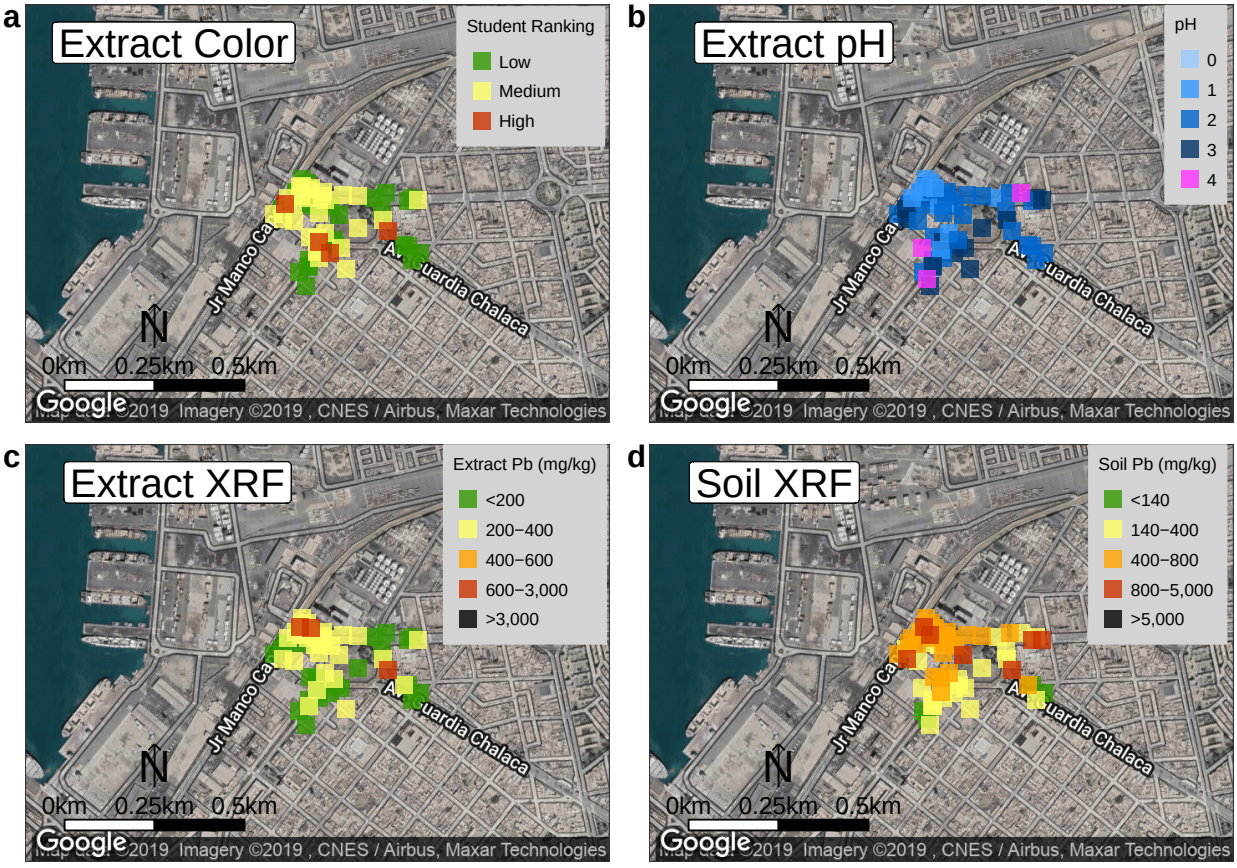

Figure 3.4: Map of sampling sites in Callao with (a) student color-ranking of the extract solution based on the field procedure color in class, (b) pH of the extract solution measured by student test strip in class, (c) extractable-Pb concentrations in solution determined by XRF on the liquid extract (and multiplied by the dilution of 1.5g soil to 15mL solution), and (d) total soil-Pb concentrations measured by XRF. Only those samples with the pH confirmed as 0, 1, 2, or 3 are shown for extract color and extract XRF.

3.4.2 Extractable Pb

For soil samples in Callao (Figure 3.4) and Cerro de Pasco (Figure 3.5), data is available for (a) student color-ranking of the extract solution, (b) pH of the extract solution, (c) extractable-Pb concentrations in solution, and (d) total soil-Pb concentrations. Due to the impact of pH on the amount of Pb released to solution, extractable-Pb concentrations measured by XRF and ranked by extract color were only evaluated for solutions in which

the pH was confirmed at or below 3. There is no pH data for Ate, and student-reported pH data from 139 samples in Callao and Cerro de Pasco confirm that 130 samples remained at or below 3, while 9 samples increased to a pH of 4 (Figure 3.6b). The extract solutions in Cerro de Pasco were much more likely to increase to a pH of 3 (48% of samples) or 4 (8% of samples) than in Callao, where 18% increased to a pH of 3 and 5% to a pH of 4 ($p<0.01$). An independent evaluation of the pH test strips based on 137 student-uploaded photos identified 97 samples at or below pH 2, 21 samples at a pH of 3, 16 samples at a pH of 4, and 3 samples at a pH of 5. It was often difficult to distinguish between pH 2 and 3, thus all samples with a pH of 0, 1, 2, or 3 were included in the analysis.

Mean extractable-Pb concentrations measured by XRF for samples with a pH of 3 or lower are 230±160 mg/kg Pb (mean±SD) in Callao and 450±610 mg/kg Pb in Cerro de Pasco, after accounting for the 10x dilution of 1.5 g soil in the 15 mL extract solution. In Callao 46% of the 63 samples extracted < 200 mg/kg Pb, 95% of samples extracted < 400 mg/kg, and only 5% samples extracted > 600 mg/kg Pb. In comparison, in Cerro de Pasco, 46% of 67 samples extracted < 200 mg/kg, 66% extracted < 400 mg/kg Pb, and 21% extracted > 600 mg/kg. There was a drastic difference between the average proportion of total soil-Pb that the field procedure extracted in Callao and Cerro de Pasco. In Callao, on average 51±30% (n=63, ±1SD) of the total soil-Pb was extracted, whereas only 22±19% (n=66) was extracted in Cerro de Pasco (Figure 3.6) and (Figure C.1), $p<0.01$). These results do not change much if samples that rose to a pH of 3 are excluded: in Callao 50±30% (n=50) total Pb is extracted and in Cerro de Pasco it is 19±23% (n=28).

3.4.3 Student-identified hotspots

In both Callao and Cerro de Pasco, students identified crucial hotspots of Pb contamination with the field procedure. In Callao (Figure 3.4), most samples were ranked as medium and highlight a central cluster of elevated Pb as well as locations along the major roads. These concentrations compare well to extractable Pb measured by XRF and total soil-Pb

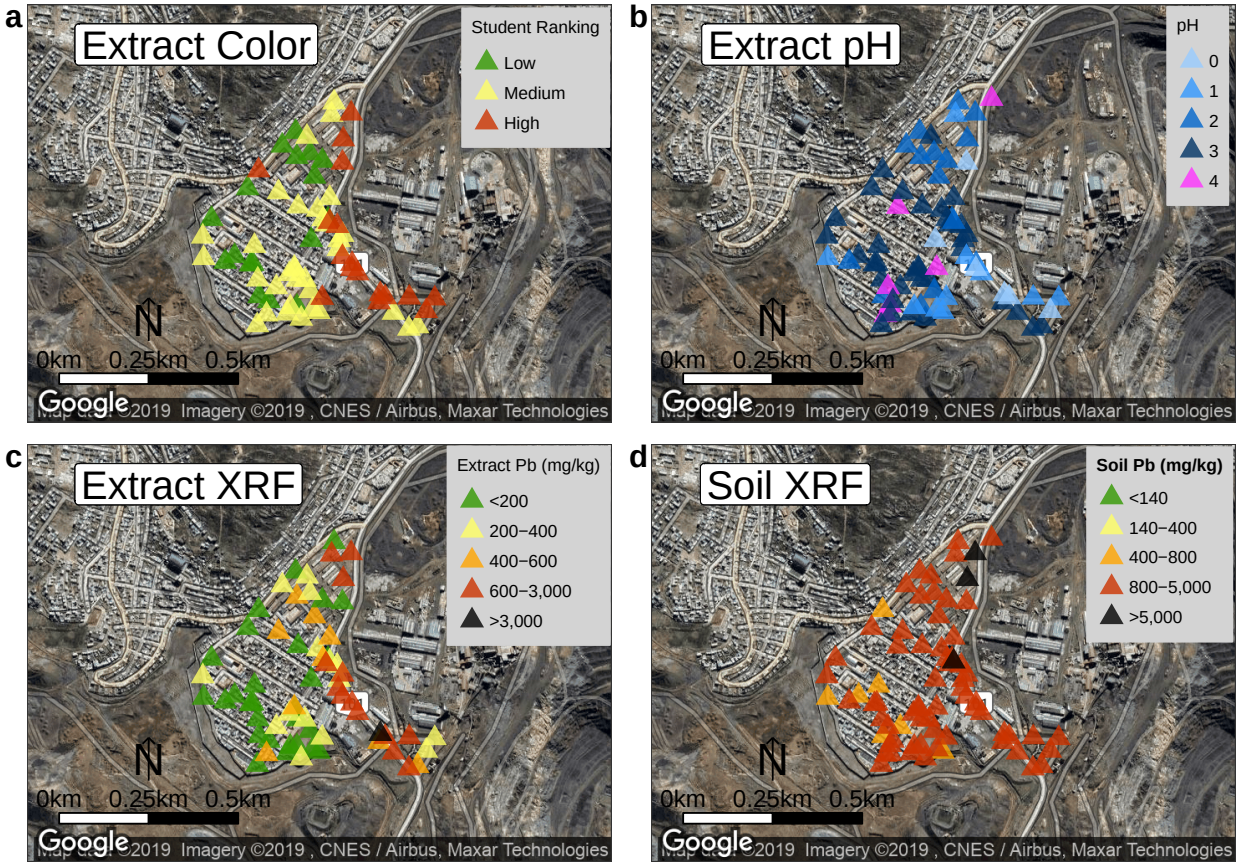

Figure 3.5: Map of sampling sites in Cerro de Pasco with (a) student color-ranking of the extract solution based on the field procedure color in class, (b) pH of the extract solution measured by student test strip in class, (c) extractable-Pb concentrations in solution determined by XRF on the liquid extract (and multiplied by the dilution of 1.5g soil to 15mL solution), and (d) total soil-Pb concentrations measured by XRF. Only those samples with the pH confirmed as 0, 1, 2, or 3 are shown for extract color and extract XRF.

concentrations to confirm the central cluster of elevated Pb concentrations. In Cerro de Pasco (Figure 3.5) the field-procedure extract color results highlight the highest concentrations in a "C" shape edge of the neighborhood closest to the ore processing plant from the open-pit mine. This is also reflected in the extractable-Pb concentrations and the location of the highest concentrations of total soil-Pb. Cerro de Pasco also had the highest percentage of soil samples increase in pH, with 8% increasing above 3 and 56% increasing above 2. While soil samples from other portions of the neighborhood did not extract as much Pb, it is important to note that the total soil-Pb concentrations were still very high.

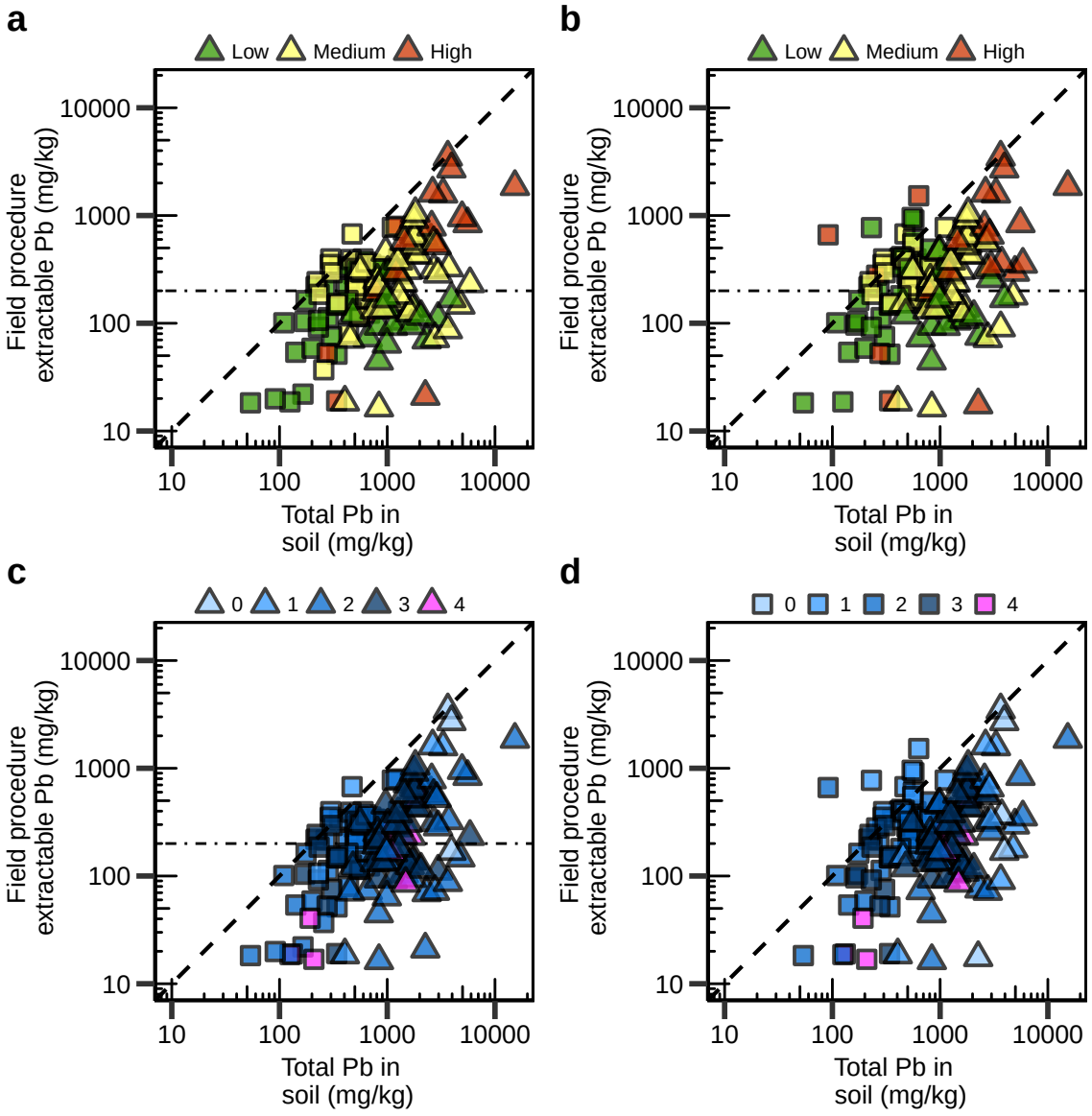

Figure 3.6: Extractable Pb as determined by XRF on the liquid, compared to total soil Pb, also determined by XRF, for samples from Callao (squares) and Cerro de Pasco (triangles). Samples shown include the data analyzed and uploaded by students (b and d), and with updated information for 39 reanalyzed samples (a and c). Symbols are shaded in (a and b) by color ranking for only those samples with the pH confirmed 3 or below and in (c and d) by pH measurement for all samples. No pH measurements were taken in Ate.

3.4.4 Assessment of student ability to conduct field test

In general, student color ranking of the field-procedure extract solution followed the trends of extractable Pb (Figure 3.7a). Of the samples that extracted the highest concentrations of Pb, more than 1000 mg/kg, all 6 were ranked high. However the following two samples,

extracting 920 and 870 mg/kg Pb, were ranked low. Of the 16 samples that extracted more than 600 mg/kg Pb, a point at which the samples should easily be detectable as "high," students ranked 63% of samples high, 19% medium, and 19% as low. All 3 samples ranked low and 2 samples ranked medium were from Callao. Photo-based color ranking generally agreed with the students, identifying 63% of samples high, 19% medium, and 13% as low (Figure 3.7b). At the other end of the spectrum, of the 36 samples that extracted less than 200 mg/kg, students ranked 64% low, 33% medium, and 3% high. Photo-based color ranking was able to better classify clear samples as low but also a classified two more samples as high, identifying 78% of samples low, 14% medium, and 8% as high.

A subset of seven samples that had extracted more than 150% of the total soil Pb originally, extracted only 15 to 55% upon reanalysis. These samples were all from Callao and include the three samples ranked low although they extracted more than 600 mg/kg Pb. An additional 32 soil samples were reanalyzed in August 2019 with the field procedure and the extract solution was measured by XRF and ICP-MS. Updating the color-ranking and extract results with these new data removes the false negatives based on extractable Pb concentration (Figure 3.7c). Precipitate ranking of the 32 samples after 24 hours resulted in better ranking of extractable Pb concentration than color ranking after 5 minutes (Figure 3.8). Extractable-Pb concentrations in solution increase between samples students rank as low, medium, and high (Figure 3.9).

Additionally, although there is no pH data available for the field-procedure extract results in Ate, students ranked 4% of the 276 samples as high, 19% as medium, and 77% as low. These results are consistent with the mean total soil-Pb concentrations of 130±110 mg/kg (±1SD) and mean extractable-Pb concentrations of 55±100 mg/kg Pb. Many of the field-procedure extracts were below the detection limit of the XRF.

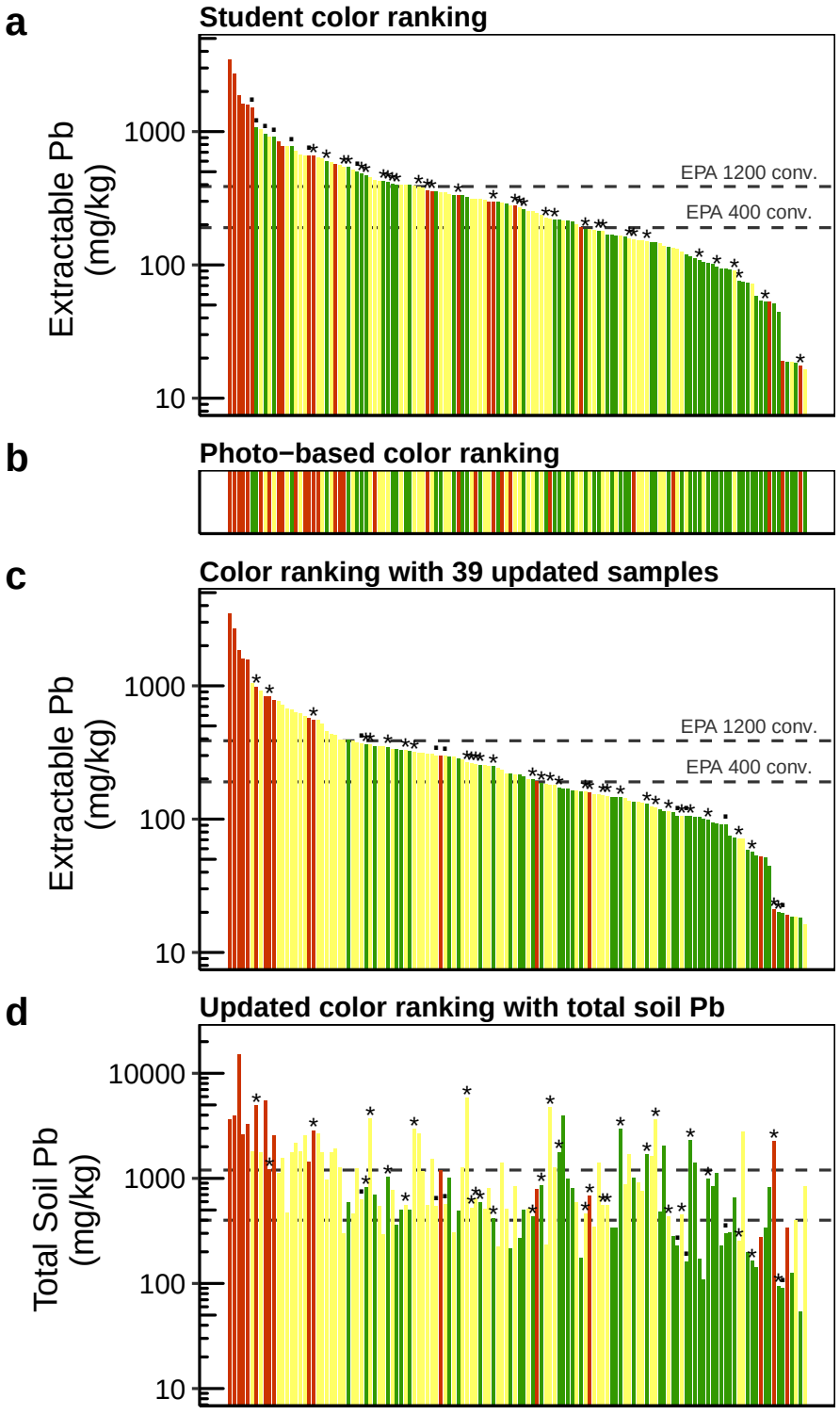

Figure 3.7: Samples ordered by extractable-Pb concentrations measured by XRF and colored in (a) by student color ranking of samples, (b) by photo-based color ranking of the same extracts, and (c and d) color ranking of reanalyzed subset (39 samples). Y-axis for (d) is total-Pb concentration in soil. Only those samples with the pH confirmed as 0, 1, 2, or 3, are shown. A square indicates that samples were reanalyzed because they extracted more than 150% Pb (n=7) and a star indicates samples were in the subset reanalyzed at Lamont-Doherty Earth Observatory (n=32).

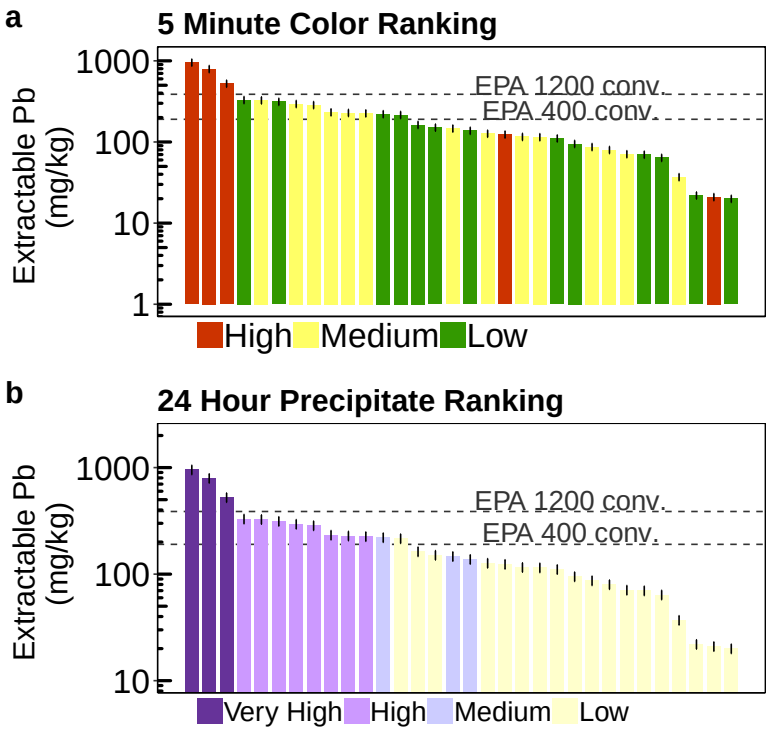

Figure 3.8: Extractable Pb, as determined by ICP-MS measurements of a subsample of 32 samples extracted and analyzed at LDEO in August 2019. Samples ordered by decreasing extractable-Pb concentration and colors represent in (a) color rank at 5 minutes of high, medium, or low, and in (b) precipitate amount visible after 24 hours as very high, high, medium, or low.

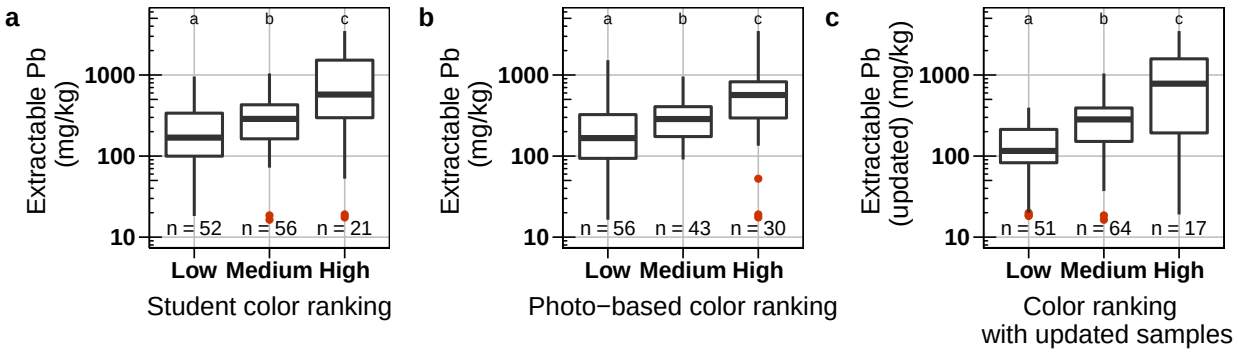

Figure 3.9: Extractable Pb, as determined by XRF, for samples ranked low, medium, and high by (a) students, (b) researcher viewing photos taken by students, and (c) combination of students and 39 updates samples. Only those samples with the pH confirmed as 3 or below are shown. No pH measurements were taken in Ate. Different letters represent groups that are statistically different ($p<0.05$).

3.4.5 Student survey results

Completed pre- and post-tests surveys are available for 135 students, from before and after participating in all of the soil lead activities. Of the nine questions asking about science interest and motivation, only the answers to two questions, "I am a motivated student," and "I excel in science," significantly increased after the activities (Figure 3.10).

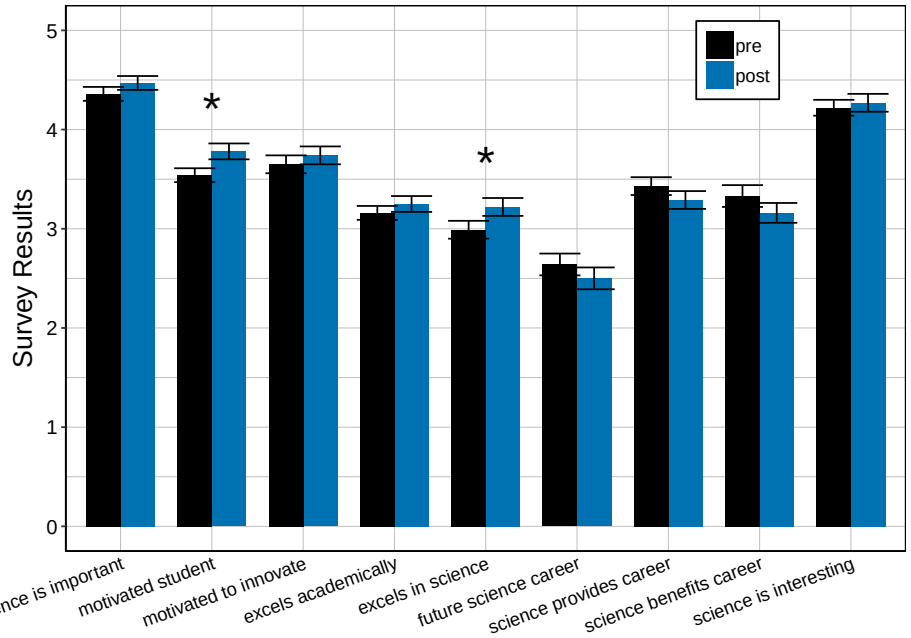

Figure 3.10: Survey results of 135 students before and after participating in the soil lead testing activities in their high school science and technology course. Mean results are shown with 1 standard error of the mean and stars indicate significance at $p<0.05$. Student responses to the questions "I am a motivated student" (motivated student) and "I excel in science" (excels in science) were significantly different based on a Kruskal-Wallis rank test.

3.5 Discussion

3.5.1 New information gained from this process

Students using the field procedure to screen soil for hazardous levels of Pb identified elevated Pb concentrations in the mining town of Cerro de Pasco and the port of Callao (Figure 3.2). While past studies in both of these areas indicated known Pb sources and elevated BLLs,

these new soil samples were collected by the students in areas relevant to them and were shared with parents to ensure that this local knowledge remains in the community. Analysis by XRF of Pb in both the original soil sample and the field-procedure extract confirmed student readings and highlighted variability in soil Pb and bioaccessibility.

Samples in Callao revealed a large range of total and extractable Pb concentrations and most extractions remained at an acceptable pH of 0, 1, 2 or 3 (Figure 3.4). Only a handful of samples exceeded the Peruvian industrial Pb standard of 800 mg/kg Pb, although most exceeded the residential standard of 140 mg/kg Pb. In Cerro de Pasco, on the other hand, the vast majority of samples exceeded 800 mg/kg Pb (Figure 3.5). The highest extractable-Pb concentrations were to the east of the sampling area, near the processing plant of the mine. This difference in soil properties is also reflected in a difference of extractable Pb: in Callao the field procedure extracted 51±30% (n=63) of the total soil Pb (±1SD), and in Cerro de Pasco only 22±19% Pb (n=66) was extracted. Extractions in Cerro de Pasco were much more likely to increase in pH to 3 or 4 (56%).

Samples collected in Ate were low in Pb concentrations, despite a nearby battery recycler 0.6 km away from the school, and 0.4 km east of the extent of the sampling areas (Figure 3.2). Four different courses participated in Ate and combined provided a large data set of soil samples around the school. It is only after this first deployment of the field-procedure that pH started to be recorded systematically. Across all soil samples, including those with no pH information or where the pH rose to 3 or 4, the proportion of extractable Pb in Ate (mean±1SD: 72±63%, median:54%, n=276) is higher than in Callao (49±31%, median:43%, n=66), and both are above that of the mining town Cerro de Pasco (21±18%, median:17%, n=72) ($p<0.05$).

3.5.2 Variability in soil and bioaccessible-Pb

The difference in Pb bioaccessibility between Callao and Cerro de Pasco is not surprising as mining soil has been found to be less bioavailable [45], and particle size plays an important

role in Pb bioavailability [32]. The mineral ore concentrate stored in Callao is composed of very fine particles that could explain the increased bioaccessibility. If we were to follow the equation in Landes et al. Figure 3, then we can convert the field-procedure extractable-Pb, corrected for the soil-to-solution ratio, to bioaccessible (IVBA) as measured by the Drexler and Brattin (DB) method and the EPA 1340, by $Pb_{DB} = (Pb_{Field-procedure} - 89)/0.34$ [78]. This can be used to calculate the in vitro bioaccessibility (IVBA) by $IVBA = (Pb_{DB}/Pb_{soil}) * 100$, which can be used to estimate relative bioavailability (RBA) by the equation described in Drexler and Brattin ($RBA = 0.8782 * IVBA - 0.028$) [46, 50].

3.5.3 Sources of inaccuracy and limitation for future use

Original comparison of Pb concentrations in soil and the student extract solution identified 11 samples that extracted more than 100% total soil Pb. A reanalysis of the 7 that extracted more than 150% determined that all of those 7 actually extract less than 100% total soil Pb. It is unclear why this error occurred, but possible student or user errors that could happen include mistakes recording the sample ID, adding the wrong amount of soil to the solution, or other as outlined below. In any case, these samples indicate that assessing whether the proportion of extractable Pb to total Pb is realistic, as well as comparing color results to total soil-Pb concentrations, is a good first order check to see if the field procedure was conducted properly.

User errors

Possible errors that could lead to an inaccurate color result as compared to extractable Pb concentrations measured by XRF include, in likely order of importance: (a) mixing up sample ID numbers, either when adding soil to the extract, when analyzing the sample, or when uploading the data, (b) not adding the correct amount of sodium rhodizonate, such as when opening the capsule and spilling some powder, and (c) not filtering the correct amount of solution. The following actions could also result in less Pb extracted by the field procedure

than expected (a) adding the wrong amount of soil to the extract solution, (b) not shaking the vial, and (c) not allowing the sample to extract for one hour.

In addition, some common errors might occur during the color analysis that overestimate Pb concentrations. These include (a) ranking solutions as medium because they turn orange or dark yellow although they remain a transparent or light color, and (b) ranking solutions medium or high because they appear dark in color but no purple or violet color is visible.

Interferences with sodium rhodizonate

Sodium rhodizonate binds with Pb to form a violet precipitate. While sodium rhodizonate also binds with other elements as outlined in Feigl and Sutter [64], the most notable elements of concern are zinc (Zn), which produces a dark gray color at high concentrations, and iron (Fe), which produces a vibrant blue color [78]. An analysis of elemental concentrations in these samples, measured by XRF, and color ranking indicated that concentrations of Pb, Zn, Fe, copper (Cu), manganese (Mn), strontium (Sr), and barium (Ba), were significantly correlated to the color (Figure C.2). Pb concentrations in the solution alone were significantly correlated to Zn, Cu, Fe, Mn, Sr, and calcium (Ca). Additionally, increased pH was correlated with Ca concentrations. In the case of possible interferences, usually identifiable by dark gray solutions, it is recommended to let the solutions sit for 24 hours and then examine the amount of precipitate that has settled at the bottom [78]. This was done for a subset of 32 samples reanalyzed in August 2019 (Figure 3.8), which confirmed that ranking samples by the precipitate amount clarifies extractable-Pb concentration. In time-limited class settings, however, this is more difficult to do and it was not done with students for this study.

Since the soils originate from mining sources, it is not surprising that Pb concentrations were correlated with other metals often found in sulfide deposits (Zn, Cu, Fe). The differences seen in the elemental correlations between samples from Callao (concentrated mineral ore storage) and Cerro de Pasco (open-pit mine) highlight these differences (Figure C.2). To

isolate the potential impact for solutions low in Pb to be ranked as high, a subset of samples with low Pb concentrations (<200 mg/kg extractable Pb) was examined. The color result remained significantly correlated with Pb, Zn, and Fe (Figure C.2), but despite these potential interferences, the vast majority of samples were still categorized correctly (Figure 3.7). One notable exception from Cerro de Pasco, sample P01B-4B09, also had an extremely high total soil-Pb concentration, but low extractable-Pb.

3.5.4 Implications for future use

This study showed the success of integrating a field procedure to screen soil in a "Science and Technology" course in three different high schools in Peru. Students successfully identified the most contaminated areas and presented these results to their communities. Instructors reported that the project was very interesting and would be helpful to reduce exposure to Pb in children and improve awareness in their community.

Simple modifications could increase the quality of student sampling and analysis. We recommend the following for future adaptations: (a) measuring the pH of the extract solution with a test strip and including this in the photo of the solution, (b) incorporating the 24 hour precipitate analysis, which could occur several days later, and (c) weighing 10 scoops of soils representative to the area to update the average dilution ratio of soil mass to extraction solution volume. As was standard procedure in this study, we also highly recommend using a phone-based app to collect geolocation and sample information during soil sampling and student color ranking, pH, and photo of the solution during sample analysis. Finally, if an XRF is available, measuring Pb in the extract solution and in the total soil sample will further confirm student test results. Assessing which samples extracted more than 100% of Pb is a good first order check to see if a mix up between sample IDs or other possible user error occurred. Discussion of analytical errors is also a helpful learning opportunity in the class and can be integrated as such.

Since Pb contamination is likely found throughout Peru [40], including smaller mining-

impacted communities that have not received much testing previously, this soil screening activity could be integrated into high schools across the country. This application is not limited to mining towns in Peru, however, as elevated exposures of Pb have been found in non-mining towns [105] and in the metropolitan area of Lima [72]. This activity could also be applied in schools globally as many communities near mines, industrial areas, and urban centers lack information about soil Pb [17]. Other good sites for deployment are those already identified as possible sources of pollution, such as through the Pure Earth Toxic Site Identification Program [101], as testing with the field procedure can help identify whether areas around schools are contaminated while increasing local knowledge and awareness about Pb contamination and methods to prevent exposure. High levels of soil Pb above 1,000 mg/kg Pb have also been found in urban cores [26], such as New York City [41, 106], and thus this method can also be integrated into high school and college classrooms in high-income countries.

3.6 Conclusion

Exposure to Pb from contaminated soil is a significant health threat for children in cities and towns throughout the world, but there are often no consistent programs to test for Pb exposure or potentially hazardous areas. Here we show that integrating a sample collection and analysis program into upper-level Peruvian high school science courses can be an effective way to generate the kind of environmental data required to identify areas to avoid and for follow-up sampling. Through this program, students collected data that is relevant to them and their communities, gained hands-on experience in their science class, and learned how to protect themselves and their communities from exposure to Pb. Recording sample location and color result with a smartphone app allows data to be easily stored, analyzed, mapped, and checked for quality control. With collaborations through a local university, XRF analysis of student-collected samples can easily increase confirm results and add information on other

elements and bioaccessibility. We propose the replication of these and similar activities in classrooms could reduce exposure by increasing collection and dissemination of environmental health data and increasing community awareness of dangerous hotspots and prevention measures.

3.7 Acknowledgments

We thank the instructors and directors of the schools for their participation to make this project possible, as well as the dedicated CREEH research staff. Funding was provided by a U.S. Agency for International Development PEER (Partnerships for Enhanced Engagement in Research) grant. This article describes the results of the first year of fieldwork for the project "Preventing lead exposure of Peruvian children from mining and battery recycling with a new field test kit" or "Lead free Kids – Peru."

Chapter 4

Elevated lead (Pb) concentrations and inventories in urban New York City

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4.1 Abstract

Soil contamination can present an important pathway for childhood exposure to the toxic metal lead (Pb) and is often overlooked in urban residential areas, where historic accumulation is concentrated in densely populated city centers. We show here first that Pb concentrations in 370 surface soils from the backyards of 76 homes in Brooklyn and Manhattan (mean:1,200±1,000 mg/kg Pb, ±1SD) far exceed the New York Soil Cleanup Objective of 400 mg/kg. The Pb content of backyard soil samples also exceeds that of 571 surface soils from tree pits and public parks (mean: 250±290 mg/kg Pb) collected in Greenpoint and Williamsburg, Brooklyn. To add a depth dimension to these patterns and attempt to understand their origin, a total of 49 cores were collected from a subset of 27 homes, and 12

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of these were analyzed for ^{210}Pb and ^{137}Cs activities. Inventories of ^{210}Pb (3.5±0.9 kBq/m^2) and ^{137}Cs (0.9±0.6 kBq/m^2) correspond to 71% and 50% of the expected radionuclide inventory, respectively. The deficits are attributed to alterations that past residents may have conducted in their yards and variations in past deposition history that reflect the unknown and complex nature of urban soils. Concentrations of Pb generally drop with depth in 30 cores (60%) but remain elevated: only 3 cores (6%) drop <100 mg/kg Pb by 20 cm and 10 (20%) do so by 40 cm. Mean uncorrected Pb inventories of 340±210 g/m^2 Pb (mean±1SD, n=12), and would increase by a factor of 1.5 to 2.5, if normalized to whole-core ^{210}Pb or ^{137}Cs inventories. All Pb inventories calculated fall well above the fallout of Pb previously calculated from a well-constrained core collected in the Central Park lake. The origin of this additional Pb input is unclear. Similarly elevated Pb concentrations in size fractions above 1 mm suggest a local non-atmospheric source, supported by confirmation of Pb concentrations in the coarse fraction (n=22) after grinding by ball mill. In other core sections (n=5) instead, a decline in Pb concentrations after acid washing the coarse fraction suggests fine Pb particles remain adhered to coarse pebble. However, individual grains picked from the cores contain up to 6% Pb and visible pieces of coal, bricks, and ash confirm some non-atmospheric sources. Regardless of the source of Pb in these urban soils, concentrations exceed health-based standards in surface soils and the heterogeneous spatial distribution indicates that testing is needed to identify contaminated areas to be covered with clean soil to reduce child exposure.

4.2 Introduction

In 1991, the U.S. Environmental Protection Agency (U.S. EPA) set the soil hazard standard for lead (Pb) at 400 mg/kg in bare soil where child play and 1200 mg/kg for other residential areas, based on the U.S. Center for Disease Control (U.S. CDC) blood Pb level (BLL) of concern of 10 μg/dL [39]. Recognizing the damaging impacts of even lower BLLs, the

U.S. CDC in 2012 switched to a reference value of the 97.5 percentile of children tested, which will be updated with the most recent National Health and Nutrition Examination Study (NHANES) [12]. One challenge of this moving health-based target is that urban soils frequently exceed several existing soil standards. California updated its residential soil screening level to 80 mg/kg Pb in 2009 based on a health risk of an increase in child BLL by 1 μg/dL [38], and New York State uses a Soil Clean-up Objective of 63 mg/kg Pb for unrestricted use, based on rural soil background concentrations, and a restricted use residential standard of 400 mg/kg Pb [37].

Lead contamination in soil can come from past and present lead-emitting sources [26] including leaded gasoline [29, 62], deteriorating lead-based paint [107], municipal waste incineration [54], smelters [108,109], mining [40], informal lead-acid battery recyclers [103] and other industrial activities [17]. While numerous studies have found higher Pb concentrations near roads, indicating the importance of leaded gasoline [43, 58, 62], analysis of sediments collected in New York City's (NYC) Central Park concluded that solid-waste incineration was the primary contributor to atmospheric Pb in the city between the 1930s and 1960s [54]. Lead, once deposited in soils, strongly sorbs to iron-manganese oxides on particles and to soil organic matter and is retained in surface soils [110]. In addition, urban soils can be heavily modified and contain fill material or debris such as coal fly ash, glass, bricks, metal, plastic, wood and more [106]. Other sources of heavy metals in urban soils are pesticides such as lead-arsenate, and construction materials [111]. This study was motivated by the need to understand the importance of additional sources of Pb for effective interventions in a major city with an industrial history in relation to a documented record of atmospheric fallout.

Concentrations of heavy metals such as Pb in urban soils have long been documented to be greater than the U.S. median Pb, or natural background level [59], of 18 mg/kg Pb [99]. A comprehensive analysis of published soil-Pb concentrations from 84 studies across 62 U.S. cities found soil Pb concentrations in cities were highest in the center and declined outwards, and the majority of studies had median and mean soil-Pb concentrations below 400 mg/kg

Pb. A handful studies did find concentrations above 400 mg/kg and 1200 mg/kg [59], notably in the Portland Peninsula of Maine (mean: 1481 mg/kg Pb) [112], in one neighborhood in Boston (mean soil Pb: 3000 mg/kg Pb compared to 600 in Boston overall) [113], and in samples collected from the sides of homes in San Antonio (mean: 1697 mg/kg Pb) [107].

In NYC data for 1,694 soil samples submitted to Brooklyn College have indicated mean soil-Pb concentrations of 600 mg/kg Pb, with 20% of samples exceeding the NYC Soil Cleanup Objective of 400 mg/kg Pb [41]. Soil samples from 68% of a subset of 197 home garden samples (median: 630 mg/kg Pb) exceeded the NYC Soil Cleanup Objective of 400 mg/kg Pb, while only 10% of 106 community garden samples (median: 140 mg/kg Pb) exceeded this limit [41]. A follow-up study found that 48% of garden samples, 7% of park samples, and 6% of public housing samples exceeded 400 mg/kg [106]. Both these studies identified areas in western Brooklyn and Queens with elevated soil Pb concentrations, and Li et al. connect local hotspots to manufacturing and industrial areas based on a 1922 map from the New York Merchant's Association [114].

The analysis of lake-core sediments collected from NYC's Central Park in 1999 established that peak atmospheric-Pb deposition between the late 1930s and early 1960s coincided with solid-waste incineration rather than leaded gasoline [54]. Four soil cores within a distance of 1 km of the lake contained ^{137}Cs inventories ranging from 2.71 to 4.49 kBq/m^2, close to the expected and decay-corrected NYC fallout of 2.93 kBq/m^2. Average soil-core Pb inventories in the soil cores were 57$\pm$14 g/m^2, normalized to whole core ^{137}Cs inventories and assuming a background concentration of 26 mg/kg. Accumulation of sediments in the Central Park lake core, based on a ^{137}Cs inventory of 4.62$\pm$0.11 kBq/m^2, resulted in a corrected Pb inventory of 64 g/m^2, and, when normalized to ^{210}Pb, 70-100 g/m^2. Uncorrected Pb inventories were 102 g/m^2 [54]. Concentrations of Pb in naturally deposited soils decrease with depth, whereas elevated or increasing concentrations with depth indicates various forms of perturbation [106].

In this study we examine Pb concentrations in surface soils and soil cores from 76 and 27 homes, respectively, in NYC. Samples were collected in Manhattan, from the Upper West

Side and Harlem neighborhoods, and in Brooklyn, from the Greenpoint and Williamsburg neighborhoods. Concentrations of Pb and inventories of Pb, ^{210}Pb, and ^{137}Cs, are compared to previously published data, and we find extremely elevated concentrations in all sampled neighborhoods. Grain size distribution, elemental ratios, radionuclide inventories, and neighborhood characteristics are examined in an attempt to distinguish possible sources of Pb contributing to the elevated concentrations.

4.3 Methods

4.3.1 Soil sample collection

Soil samples were collected from the backyards of 76 private homes (n=370) and from publicly accessible parks, tree pits, and other green areas in NYC (n=571) (Figure 4.1). Composite surface soil samples were collected in an area of approximately 0.5 m^2 with a stainless steel spoon and, if soil moisture conditions allowed, directly sieved to 1 mm using a kitchen sieve. Four to six surface soil samples were collected per yard for 9 homes in the Upper West Side (UWS), Manhattan, 4 homes in Harlem, Manhattan, and 63 homes in Greenpoint and Williamsburg (Greenpoint), Brooklyn. Surface samples from publicly accessible areas were only collected in Greenpoint; 108 of these were collected as part of an advanced Environmental Science Lab at Barnard College, mostly from tree pits, while the other 463 were collected in a systematic sampling effort paralleling backyard soil sampling in Greenpoint (Figure 4.2). Key metadata was recorded for all samples, using the smartphone app SurveyCTO [83] or KoboCollect [115], and included GPS location, photo, and site description. In a follow-up study, 49 soil cores were collected with a 2 foot AMS Soil Corer with a plastic 1 inch diameter sleeve from a subset of 15 backyards in Brooklyn and 12 homes in Manhattan. Average recovered core length for all 49 cores is 30±9.5 cm.

All home sampling visits were conducted by researchers with Human Subjects training and residents signed a consent form approved by the Columbia University Institutional

Review Board. Participants who agreed to receive a free soil test indicated how we may reproduce their soil Pb results by choosing between providing permission for us to map soil data by GPS, by the nearest intersection, or only in aggregate format.

4.3.2 Sample preparation

All home surface samples, and the subset of samples from public spaces that were not sieved in the field, were air-dried for at least 48 hours in a fume hood. Soil samples were then sieved to < 1 mm using a kitchen sieve into 20 mL scintillation vials. Core samples were cut into 5 cm intervals, weighed, and dried in an oven at 60-80°C at least overnight. Each interval was ground using a mortar and pestle, separated into fine (<1 mm) and coarse (>1 mm) fraction in 20 mL scintillation vials, and weighed. The coarse fractions of a subset of 20 core sections were ground to a fine powder by a Ball Mill (SPEX SamplePrep 8000M Mixer/Mill). A subset of 26 coarse soil fractions were also rinsed after soaking in Milli-Q DI water in a sonicator for 60 minutes to remove adhered fine particles (<1 mm) from the coarse fraction.

4.3.3 Acid digestion of soil samples

Total acid digests of a subset of 22 soil samples were done to confirm X-ray fluorescence analysis of soil metals and compare Pb isotopes (26). A 0.2 g subsample of soil hand-ground by mortar and pestle was covered in concentrated nitric acid (HNO_3) to dissolve carbonates in teflon beakers. Then samples were digested on a hotplate, first in concentrated nitric acid (HNO_3) and concentrated perchloric acid ($HClO_4$) at a ratio of 1 to 3, and then with the addition concentrated hydrofluoric acid (HF) to digest the silicates. Additional $HClO_4$ and HF were added as needed to individual samples.

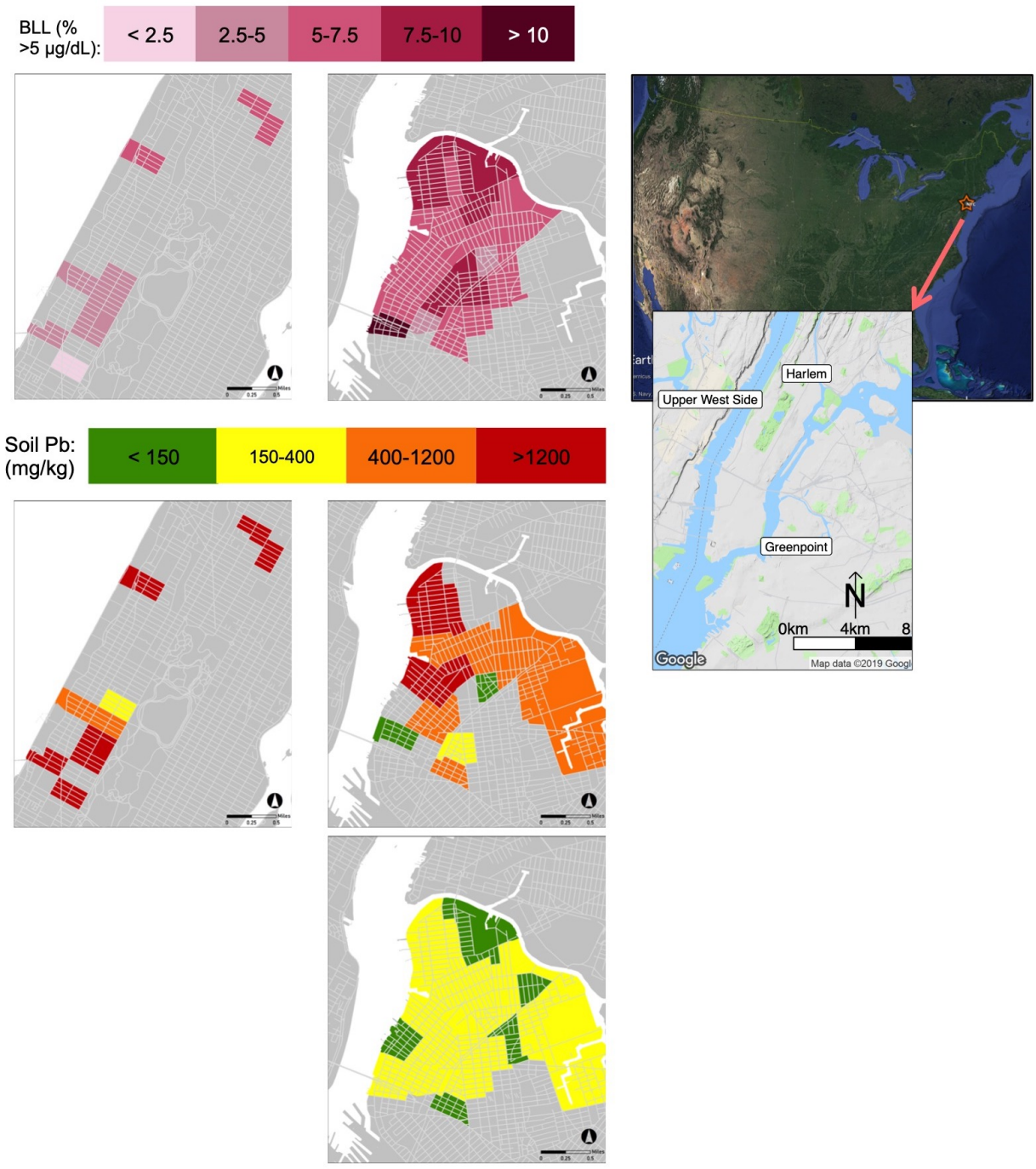

Figure 4.1: (top) Percent of children tested by census tract with blood lead levels exceeding 5 µg/dL BLL in New York City in (left) the Upper West Side and Harlem and (right) Greenpoint and northern Williamsburg. Also by census tract, mean soil Pb from (middle) home backyards and (bottom) public spaces. BLL data from Reuters, "Looking for Lead" [116] (https://www.reuters.com/investigates/graphics/lead-water/en/).

4.3.4 Instrumental analysis

All soil samples were analyzed for total Pb concentrations using a handheld X-ray fluorescence (XRF) instrument (Innov-X Systems DELTA Premium) in a benchtop stand in the laboratory. Samples in 20 mL scintillation vials were covered in plastic wrap and inverted on the benchtop stand and analyzed for 60 seconds, with 20 seconds at each of the XRF's three incident-beam energies. To better represent soil-Pb variability, each sample was analyzed three times, and the vials were inverted end-over-end between each analysis to better represent soil-Pb variability.

Results from the XRF analysis for soils were compared to U.S. National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM) soils SRM 2710 with 5,532 mg/kg Pb (mean 93±3% SD of the reference value, n=90), SRM 2711 with 1,162 mg/kg (105±2%, n=126), and SRM 2711a with 1,400 mg/kg (104±%, n=113), and SRM 2709 with 18.9 mg/kg (132±17%, n=121). Although there is a discrepancy of the low Pb XRF readings, these were not adjusted.

Analysis of total metal concentration in soils by XRF is highly correlated to acid digestion results [68] and is approved for soil by EPA Test Method 6200 [69]. In this study, a subset of samples from a complete digestion were analyzed by high-resolution (HR) inductively coupled plasma mass spectrometer (ICP-MS) (Thermo Scientific Element II). Based on these results, the following corrections were made to XRF measurements for analysis: tin (Sn) data was divided by 1.64 and zinc (Zn) was divided by 0.79 (Figure D.1). No corrections were made to XRF data for Pb (slope 0.98).

For ICP-MS analysis, data were accepted when concentrations of Pb obtained for NIST reference materials 1640A (mean recovery 107%, n=5) and 1643F (109%, n=5) were within 10% of their published values. All ICP-MS method and vial blanks contained <1 μg/L Pb. Complete digests of NIST SRM 2711a recovered 105% (n=2) Pb, and duplicates were within 3% of each other (two sets of duplicates).

4.3.5 ^{210}Pb and ^{137}Cs counting

Radionuclide activities for the isotopes ^{210}Pb and ^{137}Cs were determined by a gamma counter (EG&G Ortec, model GWL-120230) for the fine (<1 mm) fraction of 67 core intervals, with 12 complete core inventories, and three core-top samples. Unsupported ^{210}Pb, hereafter ^{210}Pb, was determined by correcting for supported ^{210}Pb estimated by measured ^{214}Pb and ^{214}Bi activities (dpm/g). Gamma-counting data for ^{137}Cs was accepted when the counting error of the following standards were within 5% of their decay-corrected published value: NIST 4350B Columbia River sediment (784± 50 pCi/kg ^{137}Cs), and GBW08304A, River Sediment, National Institute of Meteorology, People's Republic of China (2189±131 pCi/kg ^{137}Cs). Gamma-counting data for ^{210}Pb was accepted when counting error of the following standards were within 10% of their decay-corrected published value: D-standard river sediment (3838±2 dpm/g ^{210}Pb) and LGP internal and secondary standard (46.4±1.8 dpm/g ^{210}Pb).

Inventories of ^{210}Pb and ^{137}Cs activities are used to correct metal inventories in the soil cores for variations in atmospheric input. These radionuclides are often used to estimate soil erosion or sediment accumulation [117] and are useful tracers because of known atmospheric deposition. In the case of ^{210}Pb, a decay product of the noble gas radon (^{222}Rn), deposition is steady and continuous; ^{210}Pb has a half-life of 22.3 years. Inputs of ^{137}Cs, are well constrained from nuclear weapons testing in the 1960s that distributed ^{137}Cs in the stratosphere globally and activities are negligible since the 1980s; ^{137}Cs has a half-life of 30.2 years. While most studies measuring soil erosion or sediment accumulation collect radionuclide data from an undisturbed reference site, no such site was available in this study. Instead, data is compared to the average of ^{210}Pb inventories of 4.9 kBq/m^2 calculated from two studies in the northeastern United States. In the first study, a ^{210}Pb inventory of 4.1 kBq/m^2 (25 dpm/cm^2) is calculated from seven lowland soils, including a location just outside NYC that also reported the mean inventory [118]. In the second study, radionuclide data is from a soil core from Rhinebeck, NY, approximately 125 km north of the NYC, with

an estimated ^{210}Pb inventory of 5.7±41 kBq/m^2 and ^{137}Cs inventory of 3.77±11 kBq/m^2 in 1986 [119, 120]. Remaining ^{137}Cs inventories decay-corrected to 2018, when the soil cores in this study were collected, would then be 1.8 kBq/m^2. These references were also used to calculate ^{210}Pb and ^{137}Cs inventories for the Central Park lake core [54].

4.3.6 Soil inventories for metals

Soil inventories were calculated by multiplying the dry weight of each 5 cm core section by the average of three repeat XRF analyses, dividing by the 5.067 cm^2 cross-sectional area of the core, converting units to g/m^2, and adding all core sections. The average background concentration was subtracted from each XRF reading for the following: Pb: 26 mg/kg, Sn: 6 mg/kg, Zn: 80 mg/kg [54]. These calculations were conducted for both the fine fraction (<1 mm after hand grinding by mortar and pestle) and the coarse fraction (> 1 mm). For 12 soil cores with ^{210}Pb and ^{137}Cs activity data, Pb inventories were corrected by normalizing to the expected integrated fallout of 4.9 kBq/m^2 ^{210}Pb and 1.8 kBq/m^2 ^{137}Cs (9).

4.3.7 Other analyses

Neighborhood characteristics such as year of building construction and number of units per building was downloaded from NYC's Primary Land Use Tax Lot Output (PLUTO^{TM}) [121]. A subset of surface soil samples were analyzed for bioaccessible Pb following EPA Method 1340 [50] and Drexler and Brattin [46] and aggregate data were published in Landes et al. [78]. Individual sample data are highlighted in this discussion. A single high-Pb coarse grain was analyzed by laser-ablation ICP-MS.

4.3.8 Statistical analyses

Statistical analyses were performed with R Studio 1.0.136 [84] using R 3.5.1 [85]. Since soil-Pb concentrations were not normally distributed, Spearman's rank correlation coefficient was

used. Differences between neighborhoods were checked for significance using the Kruskal-Wallis test for non-parametric continuous data and a Mann Whitney U test.

4.4 Results

4.4.1 Concentrations of Pb in surface soil

The mean Pb concentration of 370 surface-soil samples collected from 76 homes is 1,200±1,000 mg/kg Pb (±1SD, median: 1000, range: 50-9200); of these samples 81% exceed the U.S. EPA soil hazard standard of 400 mg/kg where children play and 38% exceed 1,200 mg/kg Pb. Mean soil-Pb concentrations in the UWS (1400±2000, n=40) are lower than in Harlem (2600±1300, n=16) and similar to those in Greenpoint (1100±700 mg/kg Pb, n=314) (Table 4.1, Figure 4.3, $p<0.01$). In contrast, mean Pb concentrations in 571 surface soils from publicly accessible areas, mostly tree pits, in Greenpoint are much lower with a mean of 250±290 mg/kg Pb (median: 160, range: 10-3100) (Figure 4.2, $p<0.01$). Only 16% of publicly accessible samples exceed 400 mg/kg Pb and 1.5% exceed 1,200 mg/kg Pb.

Table 4.1: Descriptive statistics of surface soil-Pb concentrations collected from individual backyards (Figures 4.2 and 4.3).*UWS = Upper West Side

Neighborhood	**n**	**homes**	**Mean (±1SD)**	**Median**	**Min**	**Max**	**%>400**	**%>1200**
All	370	76	1200 (±1000)	1000	50	9200	81	38
UWS*	40	9	1400 (±2000)	590	140	9200	70	38
Harlem	16	4	2600 (±1300)	2900	900	5100	100	81
Greenpoint	314	63	1100 (±700)	990	50	5000	81	36

Mean Pb concentrations of the four to six samples collected per home averaged 1200±900, and 93% of homes had at least one sample that exceeds 400 mg/kg while 64% had at least one that exceeds 1,200 mg/kg Pb (n=76). Sample description data included whether samples were collected from (a) gardens in raised beds, (b) gardens not in a raised bed, (c) driplines, (d) unmaintained areas, (e) maintained areas, (f) areas with compost or new soil clearly added, (g) children's play areas, (h) near building walls, (i) far from building walls, (j)

the front yard, (k) near any fence, building wall, shed, or painted structure, (l) areas with reports of found debris material. There is no systematic difference in Pb concentrations for samples were collected near or far away from structures, or from maintained or unmaintained areas (Figure D.2).Samples collected from gardens in raised beds were lower than those from gardens in non-raised beds, but also samples collected not from garden areas.

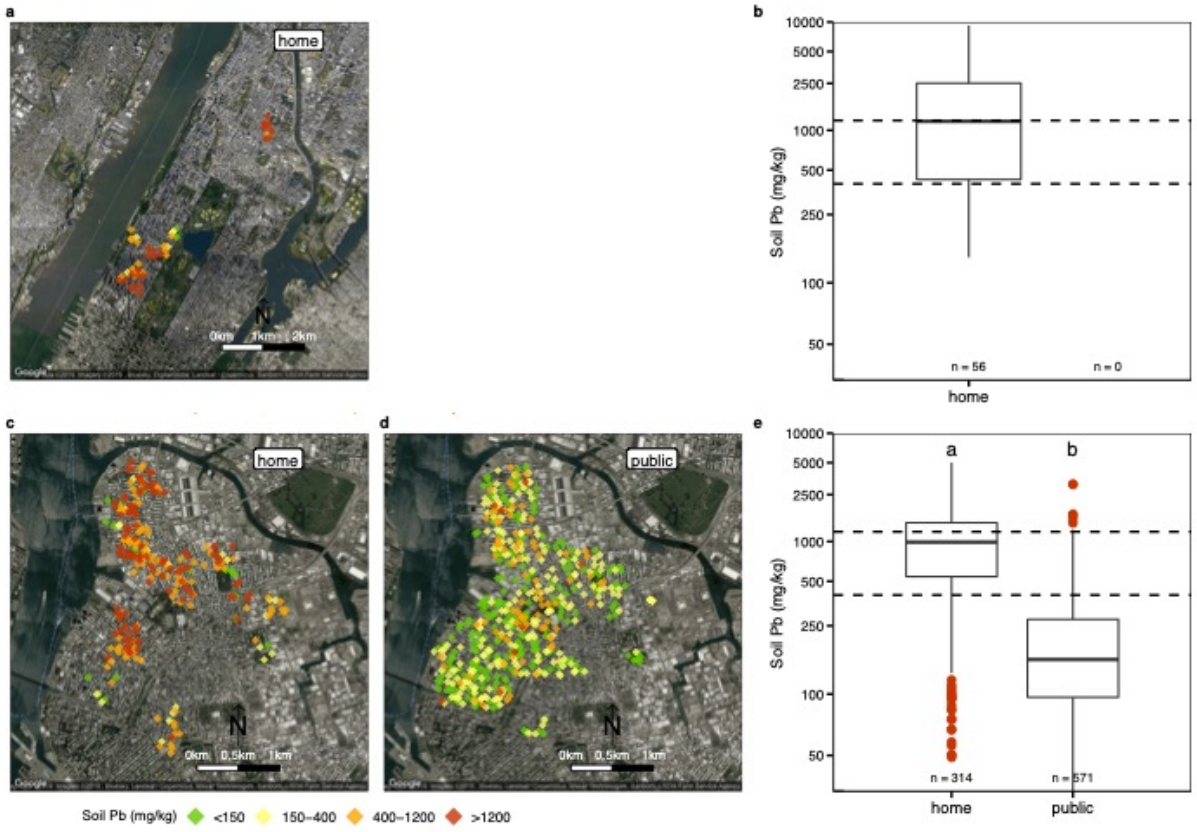

Figure 4.2: Concentrations of Pb in surface soil samples collected (a) from home backyards in Manhattan, including Upper West Side and Harlem, (c) from home backyards in Brooklyn, including Greenpoint and Williamsburg, and (d) from publicly accessible parks and tree-pits. Distribution of Pb concentrations in (b) Manhattan and (e) Brooklyn. Home samples are jittered and only included on the map if residents agreed to intersection-level disclosure on the consent form. Letters in (e) indicate groups that are statistically different ($p<0.05$).

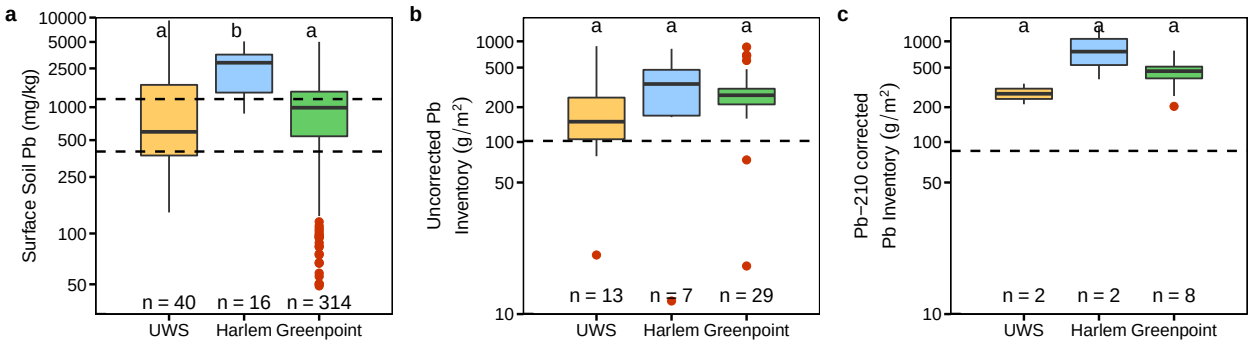

Figure 4.3: Distribution of Pb by neighborhood: the Upper West Side (UWS) in Manhattan, Harlem, Manhattan, and Greenpoint and Williamsburg (Greenpoint), Brooklyn for (a) surface soil samples (b) uncorrected Pb inventories, and (c) ^{210}Pb corrected Pb inventories. The dotted line represents in (a) U.S. EPA soil hazard standards of 400 and 1200 mg/kg Pb, in (b) the uncorrected Central Park lake core inventory, and in (c) the corrected Central Park inventory. Different letters represent groups that statistically different.

4.4.2 Depth profiles of Pb

Concentrations of Pb in the cores remain elevated throughout depth, with Pb concentrations in only 3 of the 49 (6%) cores dropping <100 mg/kg Pb by 20 cm and in 10 cores (20%) by 40 cm (Figure D.3,D.4,D.5,D.6). Average Pb concentrations are still high at 20 cm (1300±1300, mean±1SD, median: 1100, range: 40 - 7000 mg/kg Pb, n=46) and at 35 cm (mean: 700±1200, median: 130, range: 20 - 4600 mg/kg Pb, n=13). In 30 (60%) cores, Pb concentrations generally decrease with depth, and in a total of 18 cores Pb concentrations eventually drop below 100 mg/kg Pb at an average depth of 33±10 cm. In four cores (8%), two from UWS and two from Greenpoint, Pb concentrations increase drastically with depth. And in one core in Harlem, Pb concentrations never increase above 150 mg/kg Pb (Figure D.4).

4.4.3 Radionuclide inventories and profiles

Mean uncorrected inventories for the radionuclide ^{210}Pb are 3.5±0.9 kBq/m^2 (±1SD) in 12 soil cores, with an average 71±19% of the expected atmospheric deposition of 4.9 kBq/m^2. Inventories for ^{210}Pb are very similar across all neighborhoods, with (3.3±0.4 kBq/m^2 ^{210}Pb,

n=2) in the UWS, (3.7±1.2, n=2) in Harlem, and (3.5±1.0, n=8) in Greenpoint (Table 4.2, Figures 4.4 and 4.5). On the other hand, these cores contain only 50±30% of the decay-corrected ^{137}Cs inventory, with mean uncorrected ^{137}Cs inventories 0.9±0.5 kBq/m^2 (±1SD, n=12). Inventories for ^{137}Cs in the UWS (0.7±0.04 kBq/m^2 ^{137}Cs, 37% fallout, n=2) are lower than in Harlem (1.9±0.4,106% fallout, n=2) and similar to Greenpoint (0.7±0.3, 39%, n=8) (Table 4.2, Figures 4.4 and 4.5, $p<0.01$).

Core profiles show that both ^{210}Pb and ^{137}Cs reach non-detect levels by 15 to 20 cm (Figures 4.4 and 4.5). Activities of ^{210}Pb generally decrease steadily with depth, with the exception of two cores, one from Greenpoint and one from the UWS. On the other hand, ^{137}Cs activities tend to peak in 5 to 15 cm depth interval before falling below detection by 20 cm. Nine cores (75%, n=12) contain a greater proportion of expected ^{210}Pb than ^{137}Cs, and the only two cores with a greater proportion of ^{137}Cs than ^{210}Pb were collected in Harlem.

Table 4.2: Mean core (mean (±1SD)) inventories for the radionuclides ^{210}Pb and ^{137}Cs (Figures 4.4 and 4.5). Proportion of expected inventory indicated in %.

Neighborhood	**n**	**homes**	**^{210}Pb kBq/m^2**	**%**	**^{137}Cs kBq/m^2**	**%**
All	12	10	3.5 (±0.9)	71	0.9 (±0.5)	50
UWS*	2	2	3.3 (±0.4)	68	0.7 (±0.04)	37
Harlem	2	2	3.7 (±1.2)	75	1.9 (±0.4)	106
Greenpoint	8	6	3.5 (±1.0)	71	0.7 (±0.3)	39

Table 4.3: Pb inventories for soil cores of all cores and those with radionuclide data corrected to ^{210}Pb and ^{137}Cs fallout data (Figure 4.6).

Neighborhood	**n**	**homes**	**Pb g/m^2 uncorrected**	**Pb g/m^2 corrected to ^{210}Pb**	**Pb g/m^2 corrected to ^{137}Cs**
All	49	27	300 (±210)		
All	12	10	340 (±210)	510 (±360)	830 (±460)
UWS*	2	2	180 (±30)	280 (±90)	500 (±130)
Harlem	2	2	590 (±260)	950 (±800)	610 (±450)
Greenpoint	8	6	320 (±170)	460 (±180)	960 (±490)

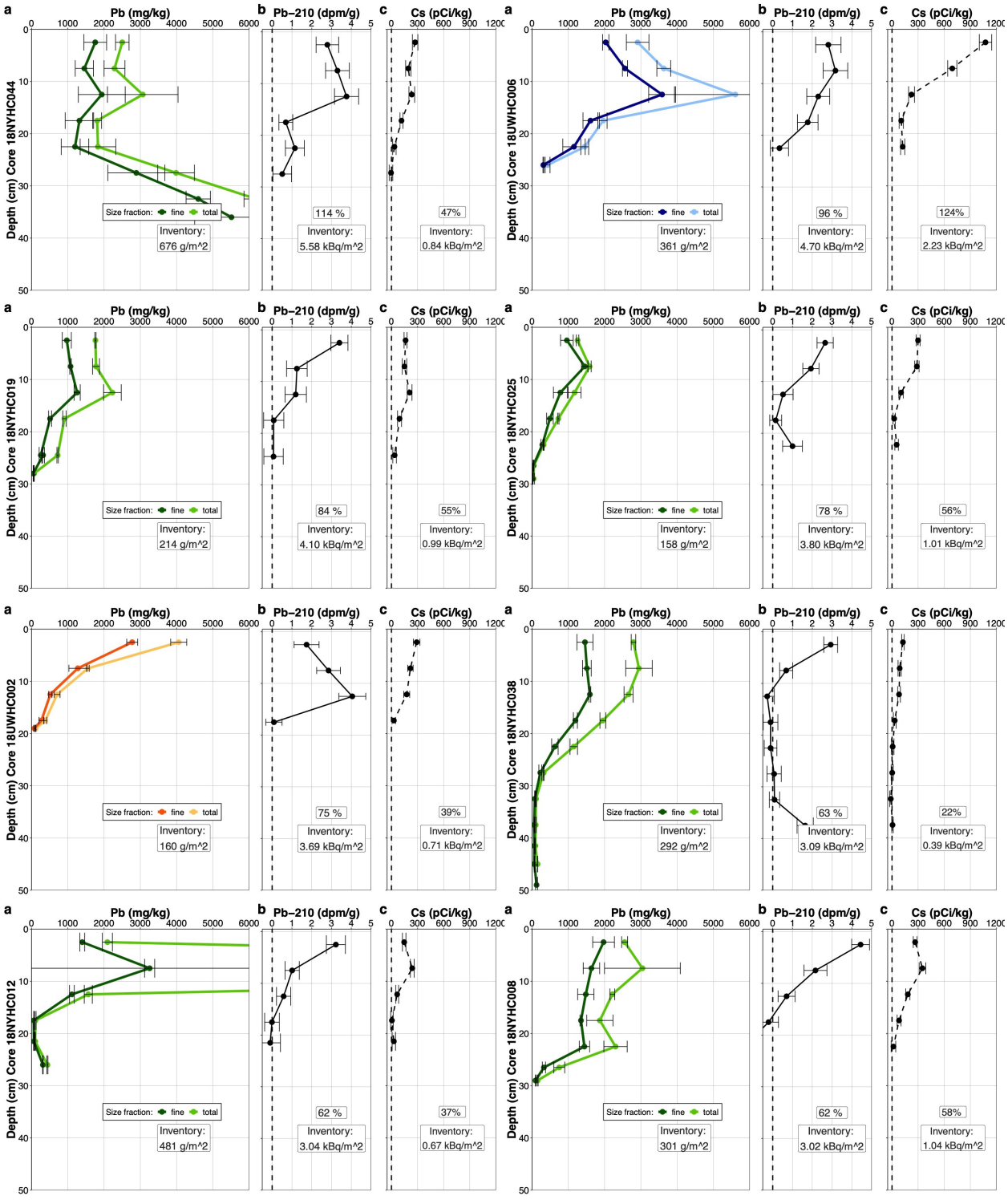

Figure 4.4: Depth profiles for cores ordered by the proportion of the ^{210}Pb inventory recovered, including (a) Pb, (b) ^{210}Pb, and (c) ^{137}Cs. Pb profiles are shaded by color to indicate neighborhood: Upper West Side (orange), Harlem (blue), and Greenpoint/Williamsburg (green). Uncorrected inventories and proportion recovered are noted in the plot.

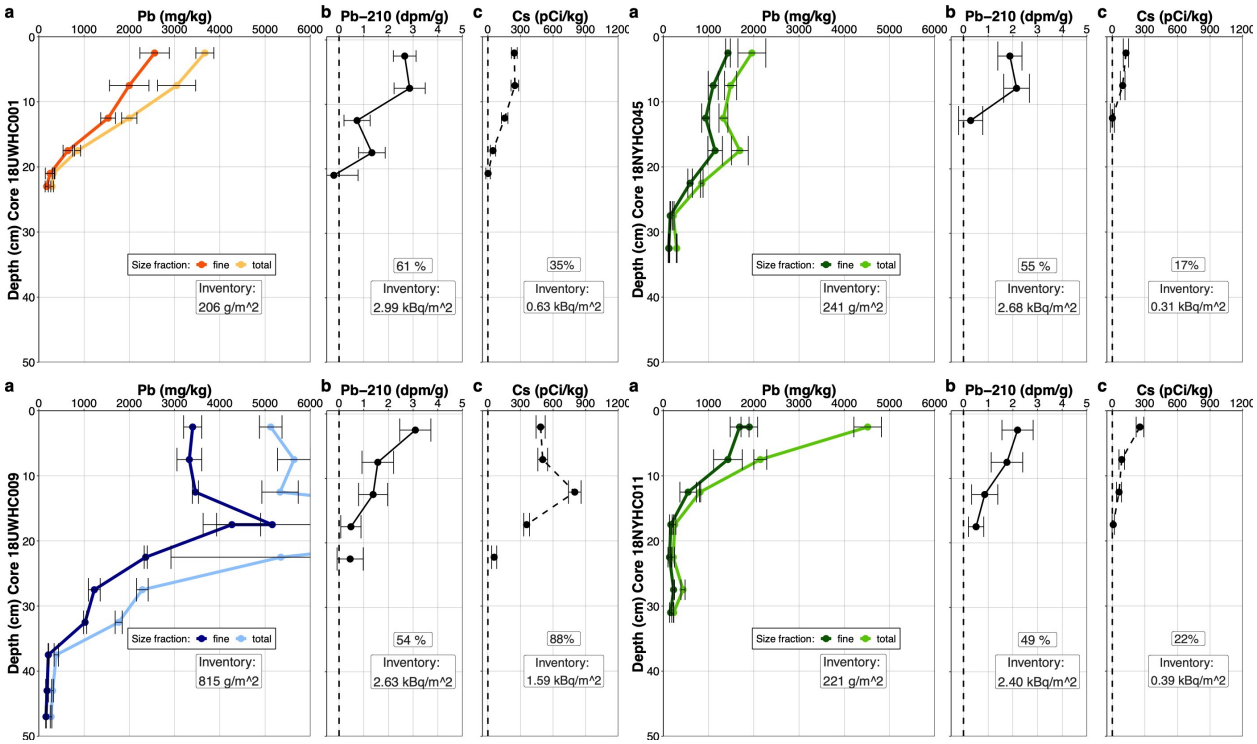

Figure 4.5: Depth profiles for cores ordered by the proportion of the ^{210}Pb inventory recovered, including (a) Pb, (b) ^{210}Pb, and (c) ^{137}Cs. Pb profiles are shaded by color to indicate neighborhood: Upper West Side (orange), Harlem (blue), and Greenpoint/Williamsburg (green). Uncorrected inventories and proportion recovered are noted in the plot.

4.4.4 Soil core Pb inventories

The uncorrected Pb inventories of 49 soil cores from 27 homes average 300±210 g/m^2 (±1SD), almost three times the uncorrected Central Park lake inventory of 102 g/m^2 Pb (Figure 4.6). Mean core inventories are similar across all inventories, with the mean in the UWS (230±240 g/m^2 Pb, n=13), in Harlem (350±280, n=7), and in Greenpoint (310±190, n=29) (Table 4.3, Figure 4.3). Core Pb inventories of only the fine fractions are 79±11% of the total core inventory, though the proportion ranges from 44% to 95%.

Corrected Pb inventories, normalized to the expected atmospheric deposition of ^{210}Pb is 510±360 g/m^2 (±1SD), eight times the corrected CP Lake inventory of 64 g/m^2 Pb. Neighborhood-level Pb inventories are, in the UWS (280±90, n=2), in Harlem (950±800, n=2), and in Greenpoint (460±180 g/m^2 Pb, n=8) (Table 3, Figures 4.3 and 4.6). Soil core Pb inventories corrected to expected ^{137}Cs fallout, are 830±460 g/m^2 (±1SD), and by

neighborhood (500±130, n=2) in UWS, (610±450, n=2) in Harlem, and (960±490 g/m^2 Pb, n=8) in Greenpoint (Table 4.3).

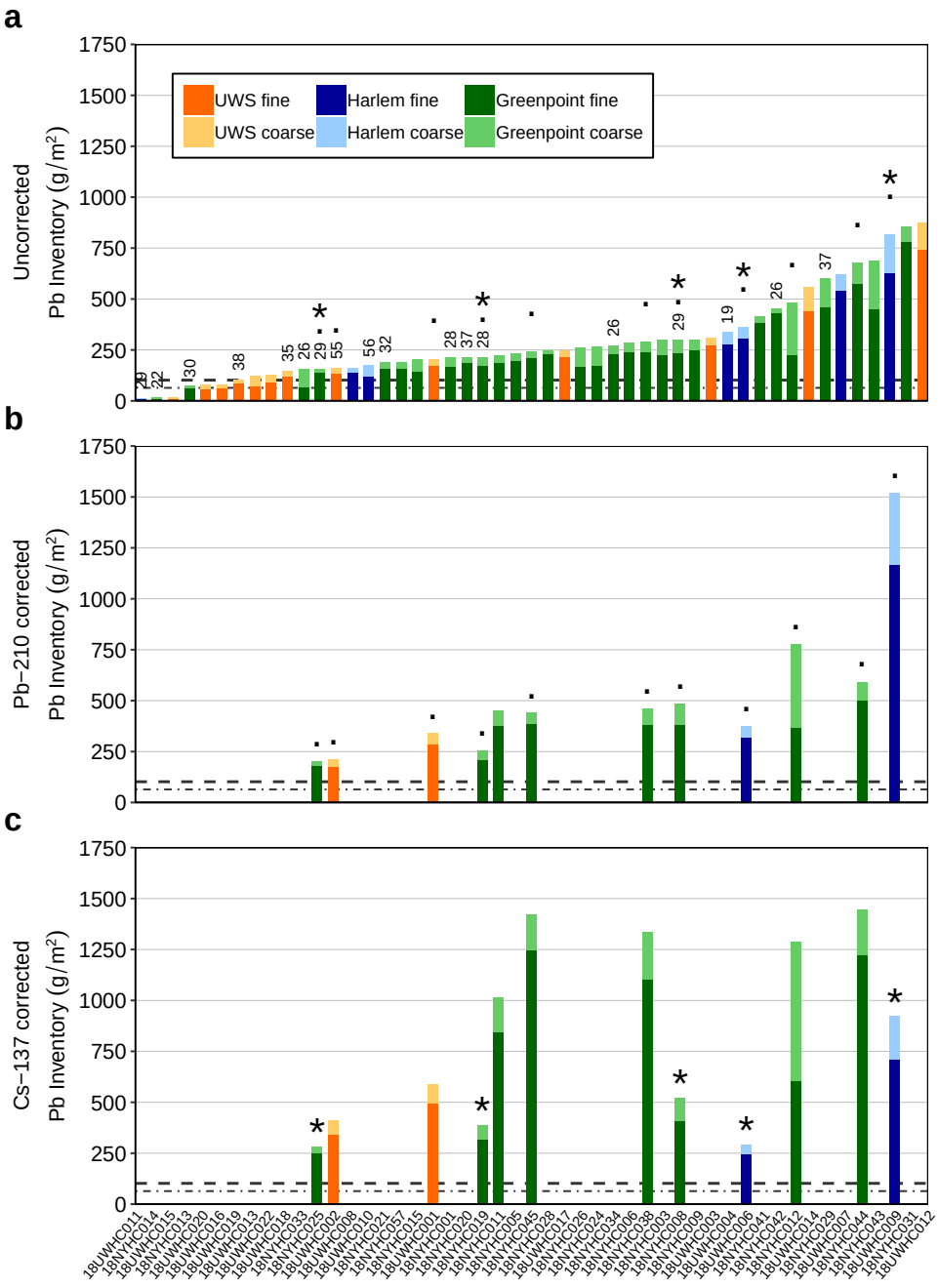

Figure 4.6: Pb inventories (a) uncorrected for 49 soil cores, (b) corrected by normalizing to ^{210}Pb inventories for 12 cores, and (c) corrected by normalizing ^{137}Cs inventory. A star (∗) indicates that the ^{137}Cs data is within 50% of the expected decay-corrected fallout, and a dot (·) indicates that the ^{210}Pb inventory is within 50% of expected inventory. The top dashed line represents the uncorrected Pb inventory of the Central Park Lake core and the dotted line represents the ^{137}Cs corrected Pb inventory from Chillrud et al. (1999) [54]. Depth of core is shown (a) in cm if Pb-concentrations drop below 100 mg/kg. All Pb concentrations were corrected by subtracting 26 mg/kg.

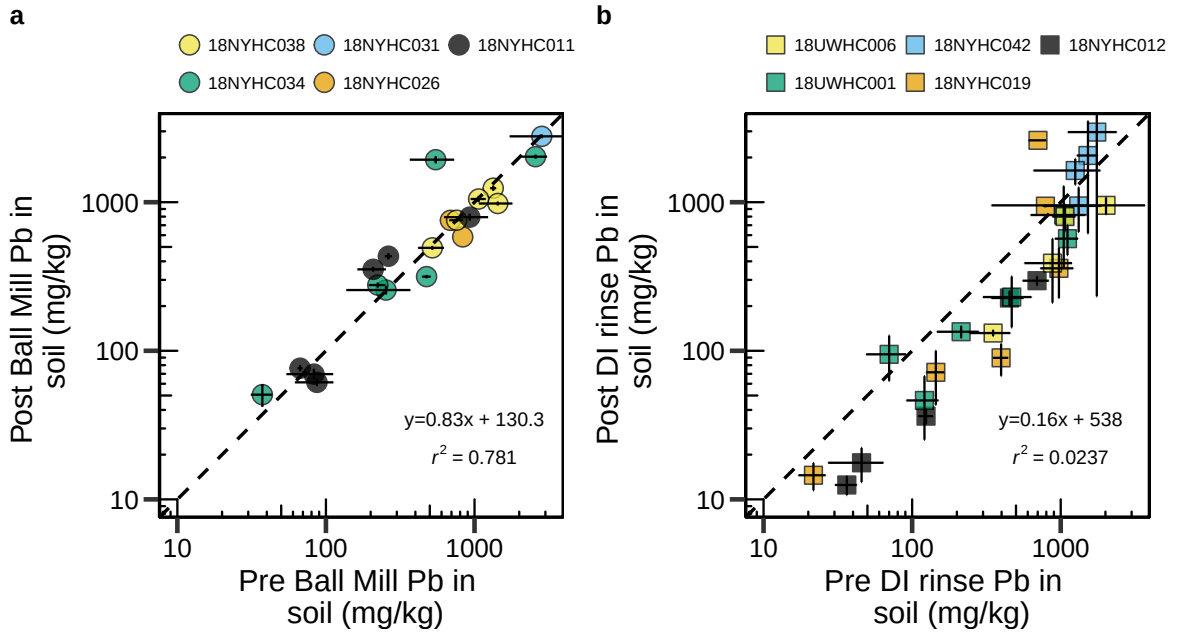

Figure 4.7: Pb concentrations in coarse fractions before and after (a) grinding by ball mill and (b) sonicating for one hour and rinsing with MQ DI water. Different samples analyzed for (a) and (b). Coarse fractions include those pebbles and rocks that remained >1 mm in size after grinding a core section by hand with a mortar and pestle. Error bars are the standard deviation of three repeat measurement by XRF, shaking the vial end-over-end between analyses. Since Pb concentration measured by XRF were largely not affected by milling (a) this supports the inclusion of Pb in the coarse fraction in calculating overall inventories. However, in (b), decreased in Pb concentrations suggest that fines do remain adhered to the coarse grains in the coarse size fraction. At higher Pb concentrations (>1000 mg/kg), Pb is not removed by sonicating and rinsing, suggesting that elevated Pb is found within the coarse grains.

4.4.5 Pb concentrations in coarse size fraction

While the coarse fraction of the cores included grains >1 mm in size that could not be hand-ground, these grains visibly retained some of the fine soil particles. Grinding 22 samples from 5 cores to a fine powder with a ball mill indicates that Pb concentrations remain unchanged for the ground and unground coarse fraction (Figure 4.7a), supporting the inclusion of the coarse fraction data in Pb inventories. The three repeat XRF analyses of the post-milling powder measure 83% of the pre-milling coarse fraction (r^2=0.78). However, Pb concentrations in 26 coarse fractions from 6 cores generally decreased after sonicating in MQ DI water for 1 hour and then rinsing with MQ DI water (Figure 4.7b). This, unlike the ball mill grinding, suggests that coarse-fraction concentrations may be biased by fine particles clinging to coarse (>1 mm) grains. At the higher Pb concentrations (> 1000 mg/kg), this

decrease in Pb is not as visible, suggesting that these coarse grains do contain high Pb. In addition, some individual coarse grains found in the cores, however, contain several thousand mg/kg Pb, with one up to 6% (60,000 mg/kg Pb) (Figure 4.8).

4.4.6 Soil core Sn inventories and profiles

Tin (Sn) is associated with Pb from solid-waste incinerator emissions at Sn:Pb ratio of 1:19 [54]. Extending the association to inventories would suggest that Pb inventories would be approximately 20 times higher than Sn inventories. This is not the case in the majority of the cores (Figure 4.9); only 9 (18%) of the 49 soil cores are within 20% of the Sn-estimated Pb inventory and 14 (29%) are within 50%. Of these, 2 cores were from Harlem and the rest were from Greenpoint; none were from the UWS. Mean uncorrected inventories for Sn are 6.6±8.1 g/m^2 and 5.2±5.6 g/m^2 (±1SD) for the total and fine fractions, respectively, with inventories in the UWS (3.6±6.8 and 2.3±3.3 (fine only) n=13), in Harlem (6.3±5.7 and 5.2±4.7 (fine), n=7), and in Greenpoint (8.2±8.9 and 6.5±6.3 (fine) g/m^2 Sn, n=29) (Figure 4.9).

4.5 Discussion

4.5.1 Implication of Pb, ^{210}Pb, and ^{137}Cs inventories

Concentrations of Pb remain extremely elevated with depth in backyards throughout NYC and Pb inventories far exceed the inventory from the lake core and four soil cores collected from Central Park in 1996 [54]. Correcting the Pb inventory by normalizing to inventories of atmospherically deposited ^{210}Pb and ^{137}Cs (Figure 4.6), only increases this exceedance. Although the Central Park cores were collected in 1996, it is unlikely that the three to eight times increase in Pb inventories occurred during the last 20 years because atmospheric concentrations have been low and more stringent regulations on paint and industrial activities have been in place.

Figure 4.8: (Top) photos of coal found in the soil cores (18NYHC024 15-19 cm and 18UWHC010 0-5 cm), and (middle) small grains that contained 6% Pb (measured by LA-ICPMS, 18NYHC012 5-10 cm) and 2% in Pb (measured by XRF) (18NYHC043 35-40 cm). One rock found in the surface soils (bottom left in Harlem) measured 1,000 to 10,000 mg/kg Pb and one (bottom right) found at 20 to 26 cm depth measured 1,000 - 3,000 mg/kg Pb (18UWHC013), depending on which side was on the surface of the XRF (gray burnt side was higher).

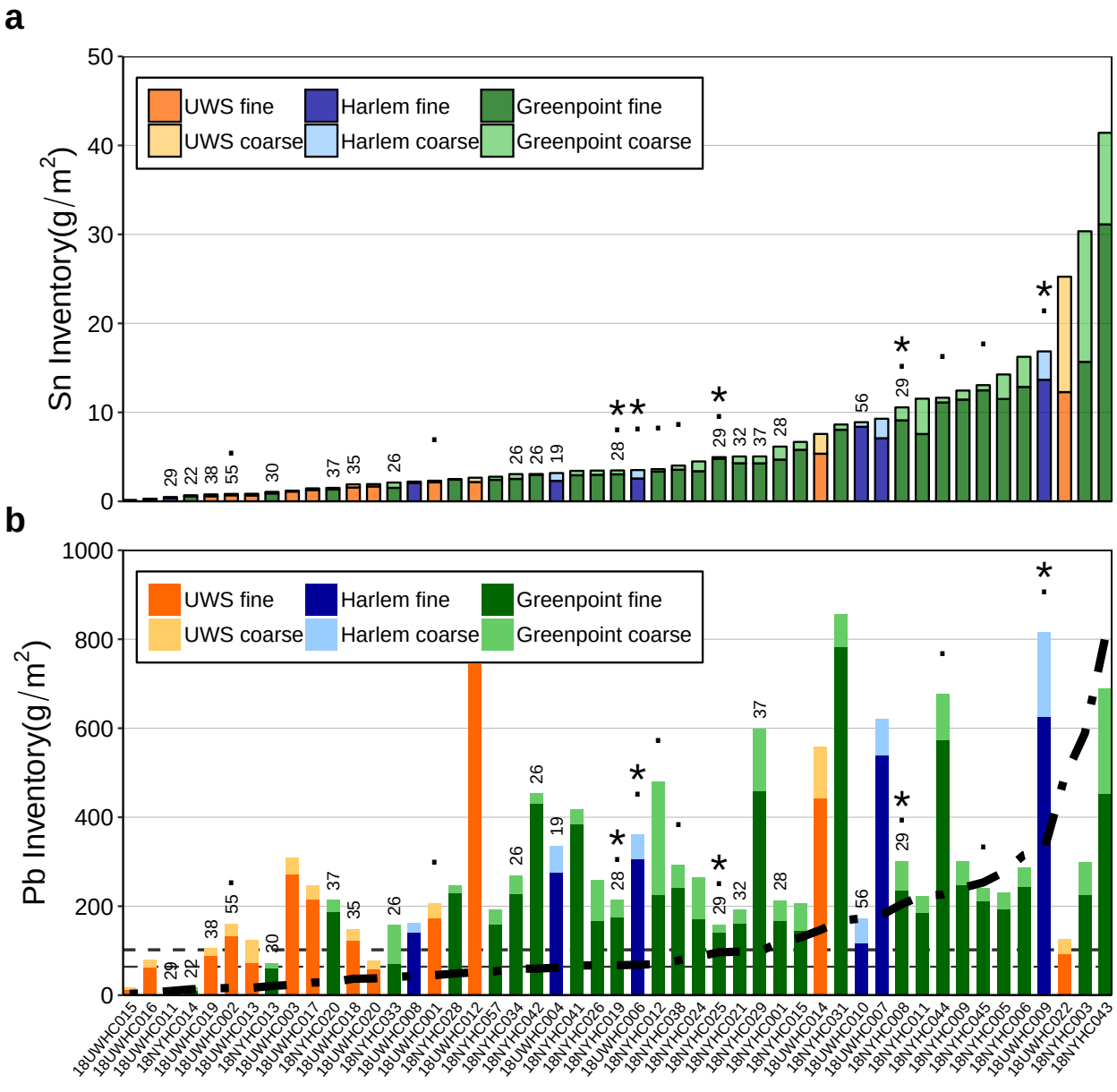

Figure 4.9: Uncorrected inventories for (a) Sn and (b) Pb ordered by Sn inventory. Solid purple line is the expected Pb inventory assuming a Sn:Pb ratio of 1:19.4, based on the ratio from solid-waste incineration as documented in Chillrud et al. (1999). A star (∗) indicates that the ^{137}Cs data is within 50% of the expected decay-corrected fallout, and a dot (·) indicates that the ^{210}Pb inventory is within 50% of expected inventory. Emissions from solid-waste incineration as documented in CP Lake sediments can only account for a fraction of the total Pb inventory. Only 9 (18%) cores fall within 20% of the Sn-based predicted Pb inventory, and 14 (29%) cores are within 50% of predicted Pb, predominantly from Greenpoint (n=12) and Harlem (n=2).

Inventories of ^{210}Pb and ^{137}Cs are often used to estimate soil erosion or sediment accumulation [117]; in an undisturbed core most ^{210}Pb is retained in the upper 10 cm and most ^{137}Cs is found in the upper 20 cm. Measurements for ^{210}Pb may be more reliable because ^{137}Cs is more mobile, with slow movement downcore, and more complex with peak fallout in the 1960s and then negligible activities starting in the 1980s, and ^{137}Cs [117]. In this study, depth profiles show ^{210}Pb concentrations reaching non-detect levels in the 15 to 20 cm core interval with maximum levels in the surface that steadily decrease with depth (Figures 4.4 and 4.5). Similarly, ^{137}Cs concentrations generally reach non-detect levels by the 15 to 20 cm or the 20 to 25 cm interval, but maximum ^{137}Cs concentrations occur at the surface in some cores and in the 5 to 10 or 10 to 15 cm interval in others. These results are consistent with both ^{137}Cs downcore mobility and the older peak of ^{137}Cs.

Soil cores from this study contain a higher proportion of expected ^{210}Pb than ^{137}Cs from fallout, though still less than the total expected, at 71% and 50%, respectively. Individual cores also contain different proportions of ^{210}Pb and ^{137}Cs, indicating different processes impacting the deposition and retention of these radionuclides in urban soils. For example, several cores contain only 58 to 59% of the expected ^{137}Cs, but 63 to 100% of the ^{210}Pb (Figure 4.6, profiles in Figures 4.4 and 4.5). A core from Greenpoint with Pb concentrations increasing dramatically at depth (18NYHC044) contained 114% ^{210}Pb and only 49% ^{137}Cs. The only two cores with a greater proportion of expected ^{137}Cs than ^{210}Pb were the two measured from Harlem, including the high-Pb core in Harlem (18UWHC009) with 90% of ^{137}Cs and only 54% of the expected ^{210}Pb.

Reasons that these cores did not accumulate the expected ^{137}Cs could be due to not capturing the peak from the 1960s because of (a) alteration of the soil, especially in the case of raised beds or other fill material, (b) spatial variability in radionuclide inventory [117], and (c) obstructions preventing ^{137}Cs deposition. In addition, we did not have an undisturbed site available to compare accumulated radionuclide inventory, but instead use previously published data for the northeastern United States. Variations in ^{137}Cs may not be uncommon

and were also reported in the Central Park soil cores, with one of the four soil cores containing 4.5 kBq/m^2, while the other three (3.1±0.9 kBq/m^2) closely matched the expected 2.93 kBq/m^2. This variation extended also to total Pb inventories: uncorrected Pb inventories ranged from 46 to 75 g/m^2 Pb, and Pb inventories corrected to ^{137}Cs ranged from 25 to 83 g/m^2 Pb [54].

4.5.2 Potential sources of NY Pb

The extremely elevated concentrations of Pb in surface soils and throughout the soil profile could come from a variety of potential sources [31], including leaded gasoline [29, 62], deteriorating lead-based paint [107], municipal solid waste incineration [54], smelting [108, 109], coal combustion, and other industrial activities [17,26]. Chillrud et al. show that solid-waste incineration was the peak contributor to atmospherically deposited Pb in Central Park [54]. Based on total and corrected Pb inventories, the majority of our cores contain more Pb than would be expected if the contribution was mainly from municipal waste-incineration; only 14 (29%) soil cores match the Pb inventory predicted by the Sn/Pb ratio of waste incineration (Figure 4.9). If the source of Pb were primarily atmospheric, we would also expect the same inventories in our soil cores as was found in Central Park.

Average backyard Pb inventories range from 3 times (uncorrected) to 8 times (corrected to ^{210}Pb) to 13 times (corrected to ^{137}Cs) the Central Park inventory. However, a plateau of uncorrected Pb inventories (Figure 4.6) between 150 and 300 g/m^2 (1.5 times and 3 times Central Park) might represent a similar Pb source for these cores. Previous studies have reported that the impacts of Pb from leaded gasoline drop off within 40 m of the roadway [43], and it is possible that the increase in backyard Pb inventory is due to closer proximity to multiple roadways. While the western edge of the Central Park lake is about 100 m from an active roadway today, in the past traffic was permitted on roads that pass within 40m of the lake. Additionally, roofs and other impervious surface areas in neighborhoods could explain an increase in backyard Pb inventory from focusing atmospheric Pb fallout.

Were this to be the case, however, we would also expect a corresponding increase in the radionuclide fallout of ^{210}Pb and ^{137}Cs, which is not observed.

The large variability in Pb inventory, as well as the large and variable fraction contained in the coarse grains, suggest that uniform atmospheric deposition of Pb as fine particles is not the only source (Figure 4.6). One likely non-atmospheric source would be deteriorating Pb-based paint. However, paint chips would have been easily ground by mortar and pestle, and thus not remain in the coarse fraction, and we did not see the expected higher Pb concentrations closer to potentially painted surfaces such as buildings, fences, and sheds (Figure D.2). Furthermore, we did not see an association with building age, however almost all of our homes were built before 1960 (Figure 4.10). This suggests Pb-based paint is not the only non-atmospheric source of Pb.

Presence of high Pb in individual grains within the coarse fraction, including a grain that contained 1.5% and one that contained 6% Pb, as well as pieces of bricks and coal, indicate that indeed other sources of Pb are likely (Figure 4.8). In four cores, Pb concentrations increased drastically ($>$ 4000 mg/kg Pb) suggesting that these yards had some type of added or fill material (Figure D.3,D.4,D.5,D.6). In one case (core 18NYHC044), the bottom core intervals were all gray and ash-like (Figure D.7), potentially indicating the dumping of combusted material also high in Pb. Historic use of coal, and potential dumping of bottom ash in backyards, was considered as another source of Pb. However, past studies show coal is not a significant contributor to atmospheric Pb [54,122] and that Pb concentrations in coal fly ash are around 100 mg/kg Pb [123]. Pieces of coal from our soil cores (Figure 4.8) measured 26 mg/kg Pb by XRF, similar to coal specimen borrowed from the Barnard Geologic Library. The concentration of 6% Pb was confirmed by laser-ablation ICP-MS in a small grain that didn't cover the XRF analysis window completely but had measured 2-3% Pb by XRF. Other rocks and grains analyzed only by XRF contained several thousand mg/kg Pb. These samples provide an insight into possible other non-atmospheric sources of Pb that could be very heterogeneously distributed throughout soils based on actions at individual properties.

Historic industrial activity may have contributed to these heterogeneous and elevated Pb inventories, especially in Greenpoint. A map of manufacturing industries in the early 20th century identify industrial zoning for "metals and metal industries" in areas that are now residential [106, 114] in Greenpoint, while Williamsburg was zoned for food products and tobacco [114]. Later, the Plan for NYC (1969) shows land use in Greenpoint and Williamsburg dominated by light and heavy industry around the East River and Newtown Creek, with pockets of low-to-high density residential zoning in the center along Manhattan Avenue in Greenpoint and Metropolitan Avenue in Williamsburg [124]. Land use in the UWS was designated as all low-medium density residential, with commercial areas along Broadway and Amsterdam Avenue, and in Harlem as high-medium density residential with commercial areas along 125th St [124]. While the UWS was described as "Sound" in a map of Neighborhood Improvement Investment strategies, Harlem, Greenpoint, and Williamsburg were noted for "Major Action," and Greenpoint and Williamsburg were marked as "Mixed Residential-Industrial" [125]. While this industrial activity may have contributed to the heterogeneity of soil Pb, it is likely not the primary source of Pb as concentrations in the residential UWS are similar to the historically industrial Greenpoint (Figure 4.3).

4.5.3 Soil Pb hazard

Regardless of the source of Pb in these urban soils, this study further highlights the health hazard posed by soils in a major urban city (NYC). The average concentrations reported here (1200±1000 mg/kg Pb, median: 1000, n=370) exceed previously published results for NYC soils (600±770 mg/kg Pb, median: 360, n=1657) [41] and most other cities [59]. Extremely concerning is the high proportion of soils that exceed 1200 mg/kg Pb (38%) and 400 mg/kg Pb (81%) (Figures 4.2 and 4.3). Median concentration of home soils is also higher than those previously reported in for NYC home gardens (median: 630 mg/kg Pb, n=197) [41] or community gardens (median: 140 mg/kg Pb [41] and median:102 mg/kg Pb [126]). The new data show that mean concentrations of soil Pb in backyards of homes are much higher

than previously thought and emphasize the need to focus on residences and backyard soil to address the public health risk from urban contaminated soil in NYC.

No clear pattern is seen between the distribution of Pb in soil samples collected near structures or in areas that appeared well cared for, e.g. maintained (Figure D.2). Pb concentrations in raised beds, however, are lower than samples from gardens in non-raised beds, but not lower than other backyard samples. It was hypothesized that raised beds would contain more new soil and compost material that would decrease total Pb concentrations. We noted however, that many of the raised beds sampled in this study were in 2-3 ft concrete edging and may have been created in part with old soil or fill material. The sample with the highest soil-Pb concentration (9200 mg/kg Pb) is from the top of a concrete raised bed that was reportedly created over 50 years ago and has remained largely undisturbed since.

Finally, as a way of assessing the relevance of these high soil Pb levels to child exposure, we compare census-tract level data for soil and child blood lead levels (BLL). The proportion of children that exceed 5 μg/dL BLL in each census tract, as published by Schneyer and Bell [116] from U.S. CDC data is compared to mean soil Pb per census tract (Figure 4.1). In Greenpoint, census tracts with the lowest child BLL (2.5 to 5 μg/dL) also have lowest mean home soil-Pb concentrations (<150 mg/kg), and the census tracts with higher BLL (7.5 to 10 μg/dL) in general have mean soil Pb of (>400 or 1200 mg/kg), although there is one outlier to the southwest, where samples collected from only one home are low (<150 mg/kg Pb). While BLLs in the UWS are lower, on average, than those in Greenpoint, mean soil-Pb concentrations are not different between these two neighborhoods (Figure 4.1 and 4.3). The building types, however, are very different between these two areas (Figure 4.10): homes in the UWS tend to have more than 20 units per home, whereas homes in Greenpoint and Harlem tend to have 4 units per home, typical of Brownstone townhouses. The number of units per home can be used to estimate building height and how likely it is that individuals have access to the backyard for direct interaction with soil, as well as how much soil might be tracked inside, or enter the home via resuspension. While neighborhood and building

characteristics may explain the lack of association between census tract Pb and child BLL data, it is important to note that no child should be playing in soils over 1000 mg/kg Pb.

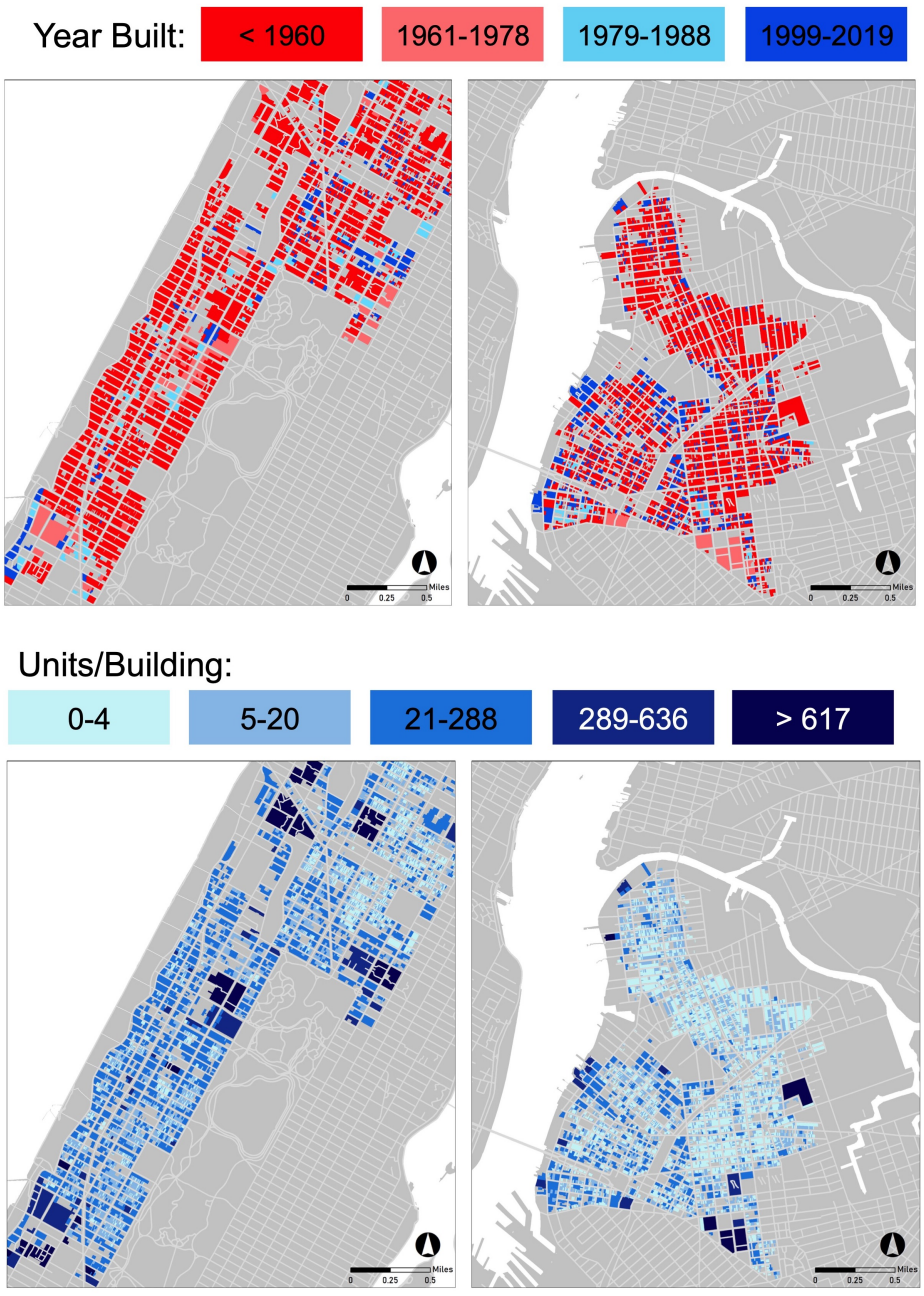

Figure 4.10: Comparison of the (top) construction year of residential buildings and (bottom) number of units per building as an indicator of building height, between the Manhattan neighborhoods of the Upper West Side and Harlem and the Brooklyn neighborhoods of Greenpoint and Williamsburg. The construction year is an indicator of lead-based paint hazards and historical accumulation of atmospheric Pb. The number of units per building is an indicator of how likely residents are to have access and interact with soil and how likely soil is to enter homes via resuspension. Figures by Maggie Calcio.

4.6 Conclusion

Elevated concentrations of Pb are found throughout New York City soils and soil profiles. Concentrations from home soil samples exceed those from public spaces and published concentrations of community garden soils and other New York soils, suggesting that any mapping of urban soils that does not explicitly test a range of samples from backyards may not capture the public health threat posed by these soils. Variable inventories of Pb, ^{210}Pb, and ^{137}Cs suggest that contributions to soil Pb are not easily constrained to a single source, and Pb inventories exceeding the integrated atmospheric contributions imply non-atmospheric contributions are also important. Additionally, elevated Pb concentrations in the coarse fraction and grains of up to 6% Pb, reveal that non-atmospheric sources are not limited to paint but may include industrial waste and other fill material. The Pb concentrations in surface soils tested in this study are extremely high and are not safe for child play areas. We encourage all residents with access to a backyard to test their soil for Pb, especially in areas where young children play. In addition, we recommend expanding programs to provide and distribute clean soil such as the Pure Soil program from NYC's Environmental Remediation Program.

4.7 Acknowledgments

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Clare McGillis, Afsana Akter, Sidney Rojas, Sara Oritz, the students from Brian Mailloux's Water Sanitation and Health Course. This work was partially supported by NIEHS SRP grant P42 ES010349.

Part III

Conclusions

Although the negative health impacts of Pb are well established and exposure to Pb from contaminated soil poses a significant health threat for children, screening soils for Pb is not common in residential areas throughout the world. Testing soil for Pb is likely to become more important as high level exposures are eliminated and the health impacts of low level exposures become better characterized. In chapter one, I present a new field procedure to screen soils for hazardous levels of Pb that is well suited for use by local health departments, citizen scientists, concerned parents, or community groups without access to a laboratory. I find the kit extracts about one-third the amount of Pb extracted by approved bioaccessibility methods and can thus be used to identify the most hazardous concentrations of Pb. If a kit derived from this method is produced in large quantities its costs could be decreased below the US$5 per samples for use on a larger scale to identify Pb hotspots.

In chapter two and chapter three, I share two different deployments of the field procedure finding in both cases that the use of the method helps identify important new soil Pb information in Peruvian communities. In chapter two, I show parents using the procedure in four small mining-impacting towns identify an additional hotspot that had been missed by a systematic roadside Pb mapping. Available BLL data, along with survey Pb information, reveal no clear relationship between soil samples and child BLL, but parent shoe and clothing cleanliness was related to BLL and could link behavior to the exposure of children to soil and dust Pb. I sugget that parent cleanliness may therefore be a valuable target of educational interventions, possibly as part of a soil screening to identify hotspots of Pb contamination. Hundreds of similar towns exist where children may be exposed but there is no environmental or exposure data. In this chapter I show that parents are motivated and capable of collecting soil samples using a simple field procedure to identify these areas of hazardous soil Pb.

In chapter three I show that integrating a sample collection and analysis program into upper-level Peruvian high school science courses can be an effective way to generate the kind of environmental data required to select areas for follow-up sampling. Through this program, students collected and analyzed soil samples in their science classes, gaining hands-on expe-

rience and learning how to protect themselves and their communities from Pb. Recording sample location and color result with a smartphone app allows data to be easily stored, analyzed, mapped, and checked for quality control. Since there are often no consistent programs to test for soil Pb, I propose the replication of these activities in classrooms could reduce exposure by increasing environmental health data and increasing community awareness of hotspots and prevention measures.

Finally in chapter four I show extremely high Pb concentrations are also found in soils and soil profiles in New York City homes. Contamination in home soil samples far exceed those from public spaces, implying that any mapping of urban soils that does not explicitly test home samples may not capture the public health threat posed by these soils. In addition, variable inventories of Pb, ^{210}Pb , and ^{137}Cs suggest that contributions to soil Pb are not easily constrained to a single source, and Pb inventories exceeding the integrated atmospheric contributions imply non-atmospheric contributions are also important. Concentrations of Pb in grains of up to 6% Pb indicate that non-atmospheric sources are not limited to paint but may include industrial waste and other fill material.

4.8 Overall implication

Lead concentrations in soils are very heterogeneous and elevated concentrations hazardous to human health exist around the world, from urban backyards in New York City to small mining-impacted towns in Peru. In this dissertation, I outline a new field procedure for first-order soil screening by the general public and then show how it can be effectively implemented in Peru with parents in collaboration with the local health center and with high school students in collaboration with educational institutions and science teachers. Exposure to Pb is entirely preventable, but testing is required to identify this environmental hazard; I strongly recommend that all residents, especially those with young children, test their soil for Pb.

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Appendices

Appendix A

Supporting Information for Chapter 1

A field procedure to screen soil for hazardous lead

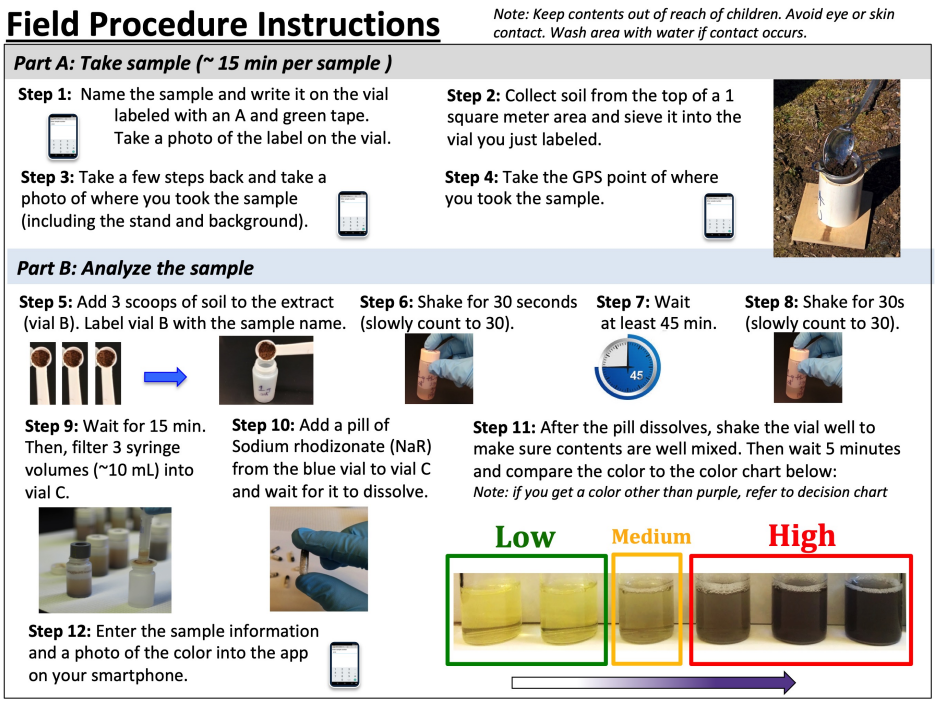

Figure A.1: Field-procedure instruction sheet with color guide as provided to people using the procedure in the current form in pilot studies.

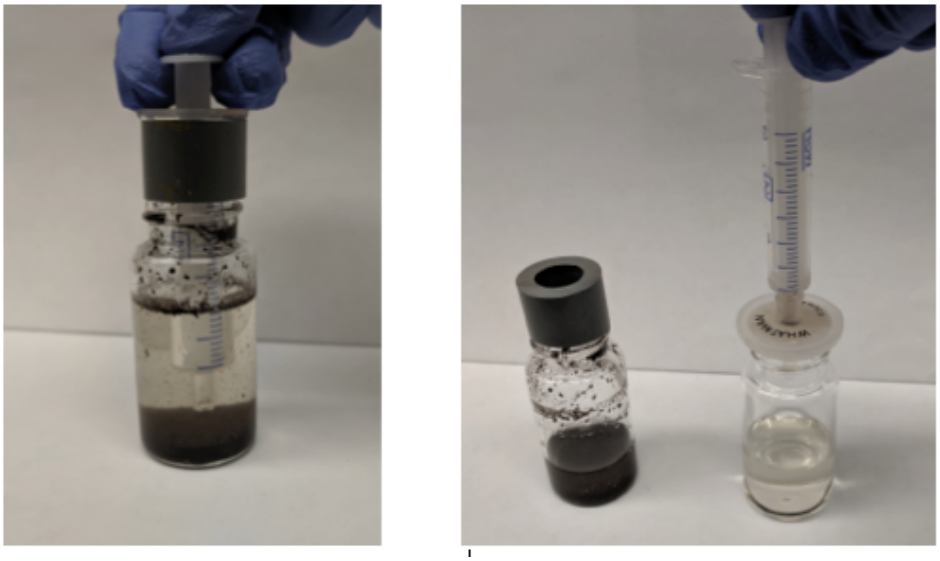

Figure A.2: Close-up photos of step 9 from Figure A.1: filtration of extract solution with syringe, spacer, and syringe filter into a new clear vial.

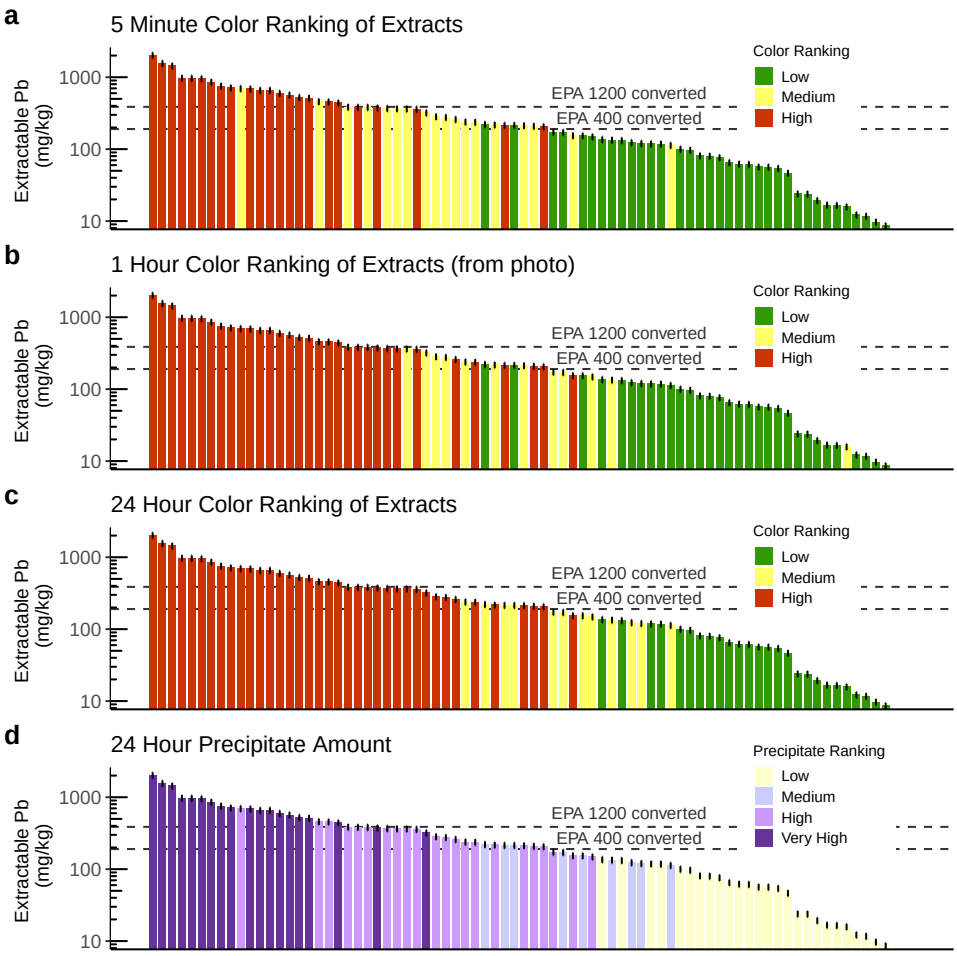

Figure A.3: Color ranking of field-procedure extract solutions as determined at (a) 5 minutes, (b) 1 hour, and (c) 24 hours, and (d) the precipitate ranking at 24 hours. Extractable-Pb concentrations were measured by ICP-MS and multiplied by the dilution factor of the soil-to-solution ratio. Color rankings are compared with EPA soil screening levels of total Pb converted to the amount of Pb extracted by the field procedure based on 71.5% IVBA and the equation in Figure 3 (400 → 190 and 1200 → 387 mg/kg Pb).

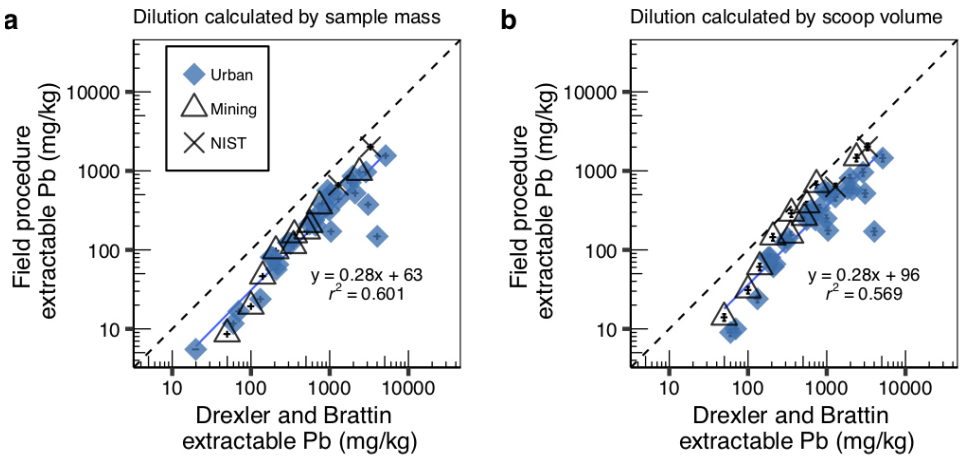

Figure A.4: Field-procedure extractable Pb compared with Drexler and Brattin extractable Pb when the field-procedure dilution is calculated by (a) the sample mass of the three scoops, and (b) the sample scoop volume with the assumed mass of 1.5 g. Only samples from 2017 are shown because these samples have both soil mass and scoop data; earlier iterations have soil mass data only. Data in (a) is a subset of samples from Figure 3 but the best-fit line differs because of the reduced sample number and concentration range.

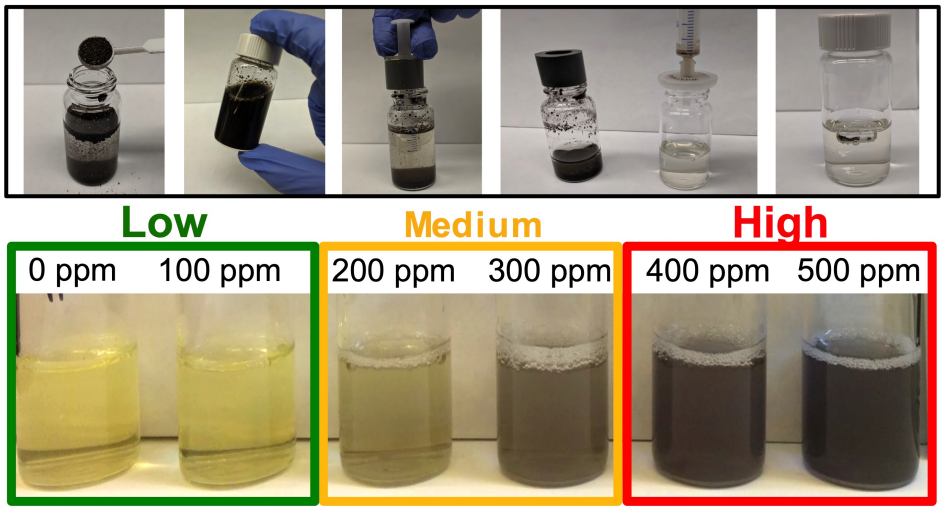

Figure A.5: Cover art from Analytical Chemsitry paper with photos depicting key steps of the field procedure and color results.

Appendix B

Supporting Information for Chapter 2

Does involving parents in soil sampling help identify causes of child exposure to lead? A case-study of community engagement in mining-impacted towns in Peru.

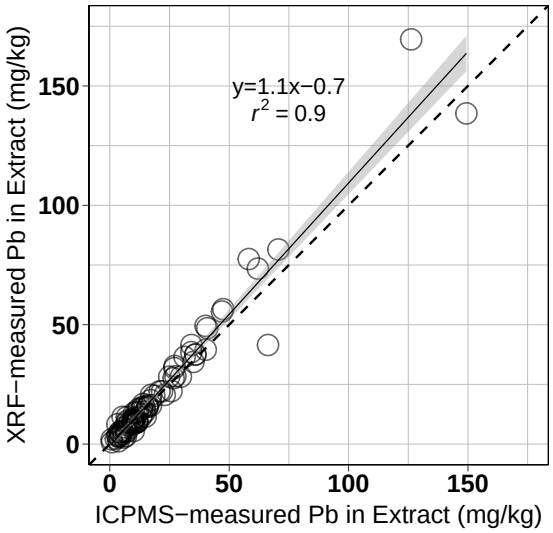

Figure B.1: Blank-corrected XRF measurements of Pb in extract solution collected in the field immediately after extraction compared to ICP-MS measurements of the same solution in the laboratory several months later. The dotted line is the one-to-one line.

Figure B.2: Instruction sheet including all field procedure steps for parents collecting and analyzing soil samples. Parents received this or a similar version that focused only on the steps Part A and Part B that they were completing on their own.

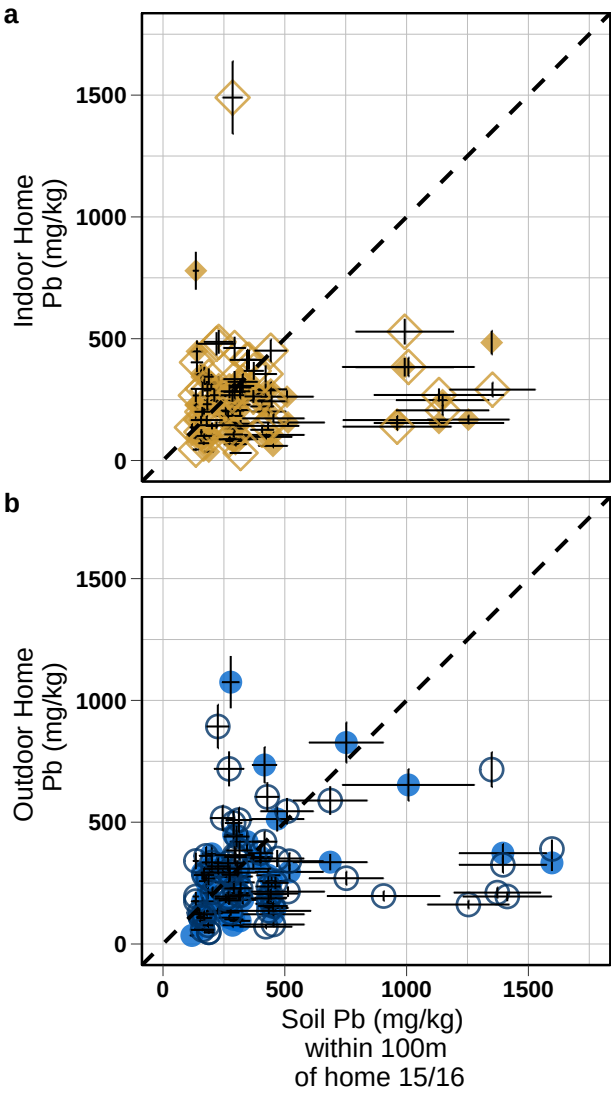

Figure B.3: Pb concentrations within 100m of the home compared with home soil samples collected (a) indoors and (b) outdoors. Closed symbols indicate samples collected during Survey 1, and open symbols indicate samples from Survey 2. Lead concentrations in dust and soil measured by handheld X-ray fluorescence in July-September 2015. Error bars of home Pb samples are 10% and error bars of the soil Pb within 100m of the home is the standard error of the number of measurements.

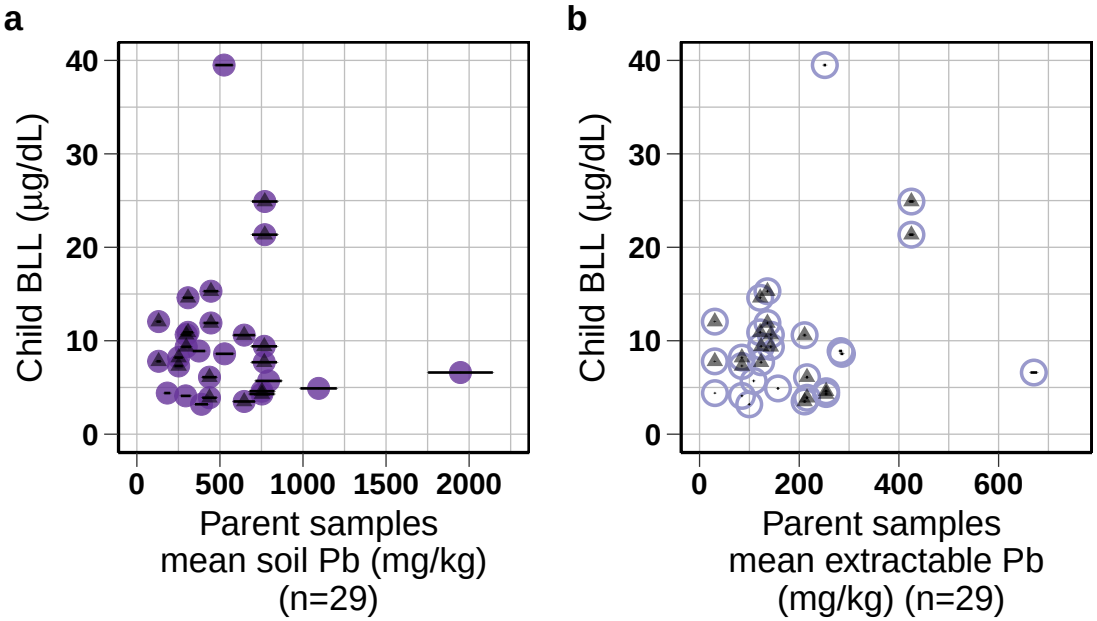

Figure B.4: Child BLL levels with (a) mean soil Pb from samples parents collected where their children play, and (b) mean extractable Pb from those same samples. All children BLL are shown: if a parent had more than one child, then parents' soil samples are repeated. Small black triangles inside the circles indicate that a child had a sibling. Pb concentrations measured by XRF for total Pb in soil and by ICP-MS for extractable Pb. Error bars shown are 10% for both.

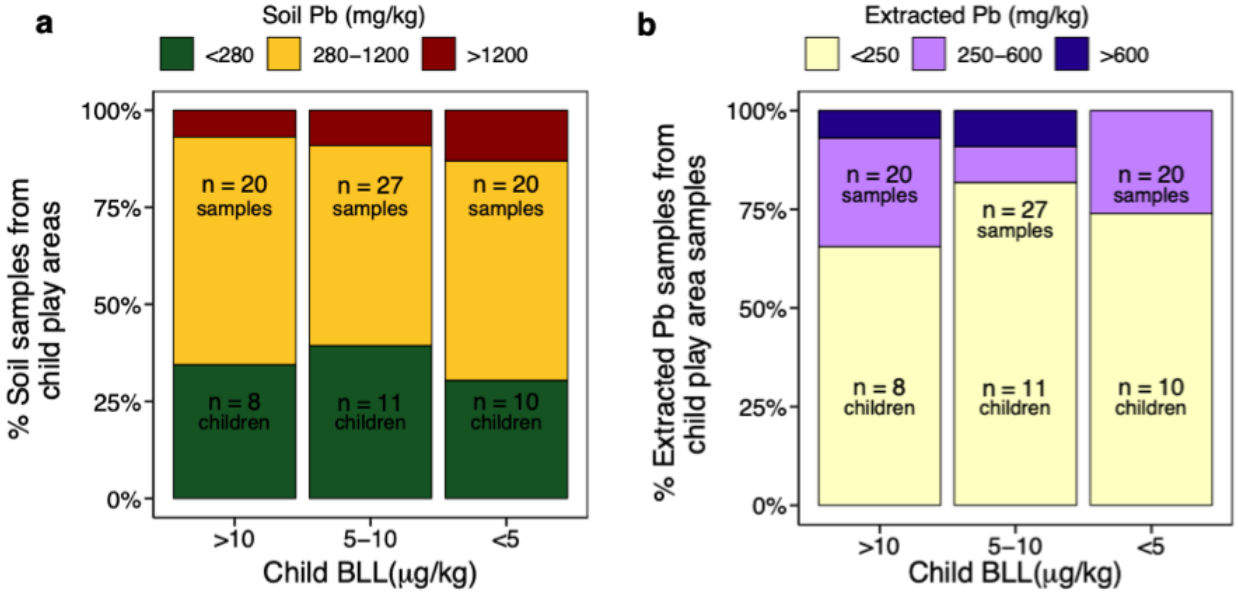

Figure B.5: Parent field kit samples by child BLL category for (a) total Pb in soil samples and (b) extractable Pb from the same soil samples. All child BLLs are shown: if a parent had more than one child, then the parents' soil samples are repeated. Pb concentrations measured by XRF for total Pb in soil and by ICP-MS for extractable Pb.

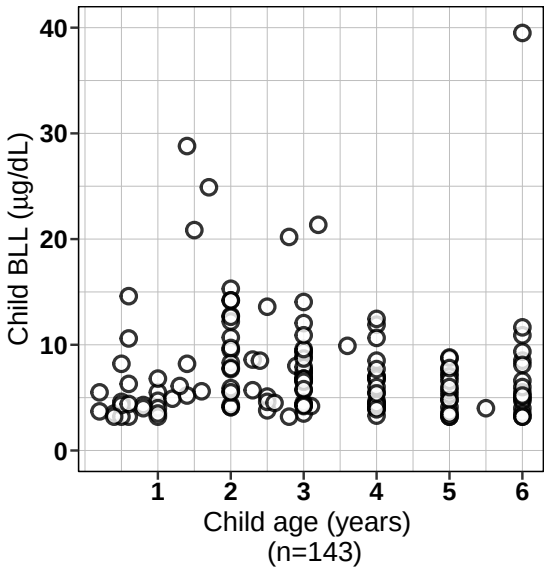

Figure B.6: Child BLL by age. All children with BLL information shown: if a parent had more than one child, then both children are shown.

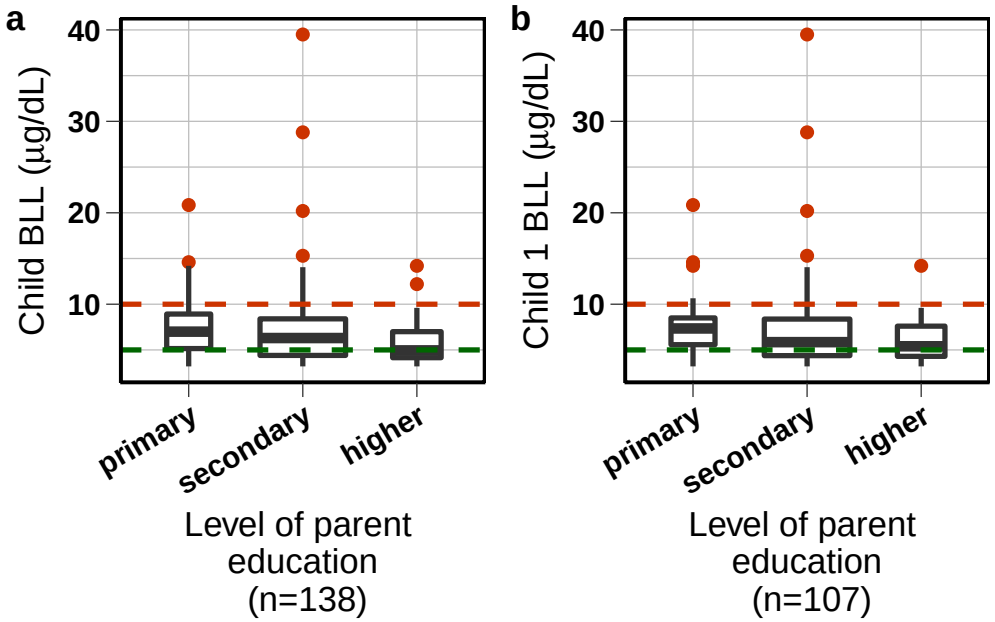

Figure B.7: Child BLL by parent education including (a) all children with BLL information, in which case if a parent had more than one child, then both children are shown and parent education level is repeated; and (b) only the youngest child BLL information of each parent is shown.

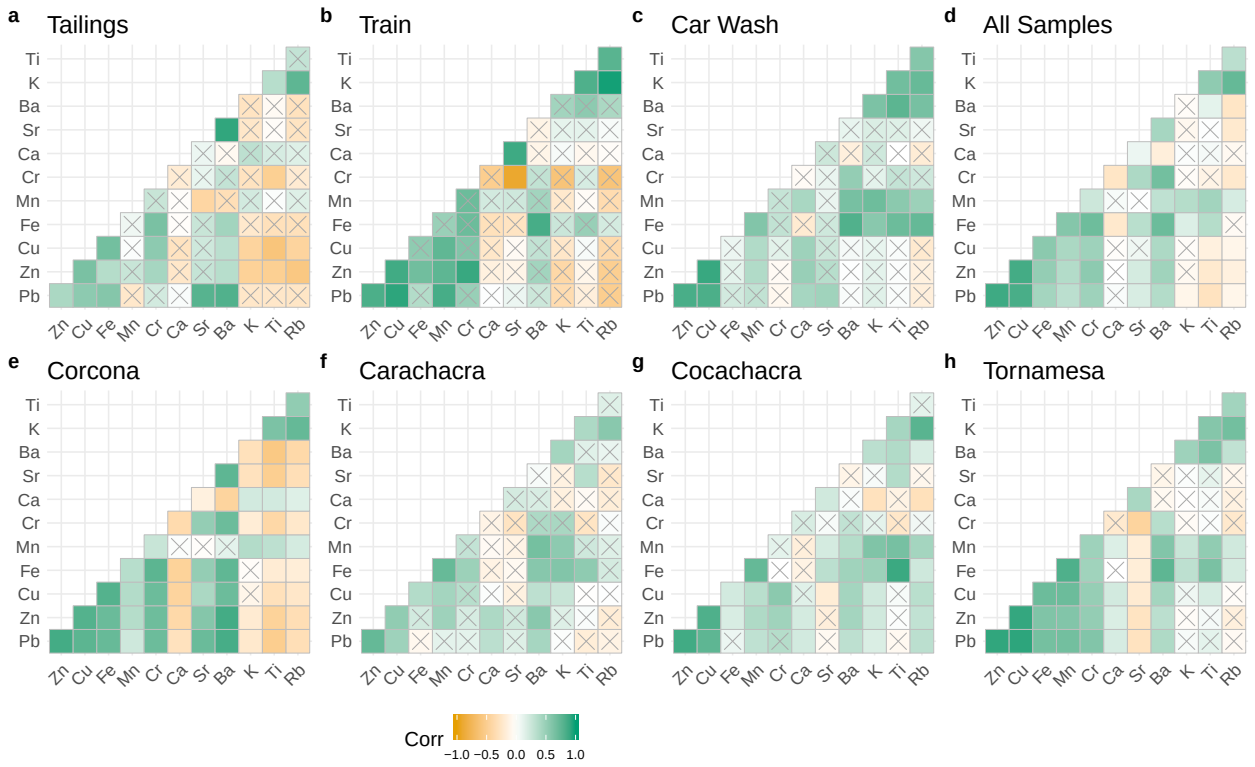

Figure B.8: Spearman rank correlation matrices of elements analyzed by the XRF. Accurate XRF analysis of elements was confirmed by comparing to XRF analysis of NIST soil standards. Values below the limit of detection (LOD) were included as 1/2 their LOD value. Arsenic (As) was not included because of the known interference between the As the Kα emission energy of 10.543 and the Pb Lα emission energy of 10.551, if one element is more than 10x the other (https://www.olympus-ims.com/en/applications/xrf-technology-analysis-arsenic-lead-soil/). Variations between towns are visible, reflecting different geochemical make-ups. Gray X indicates the correlation was not significant.

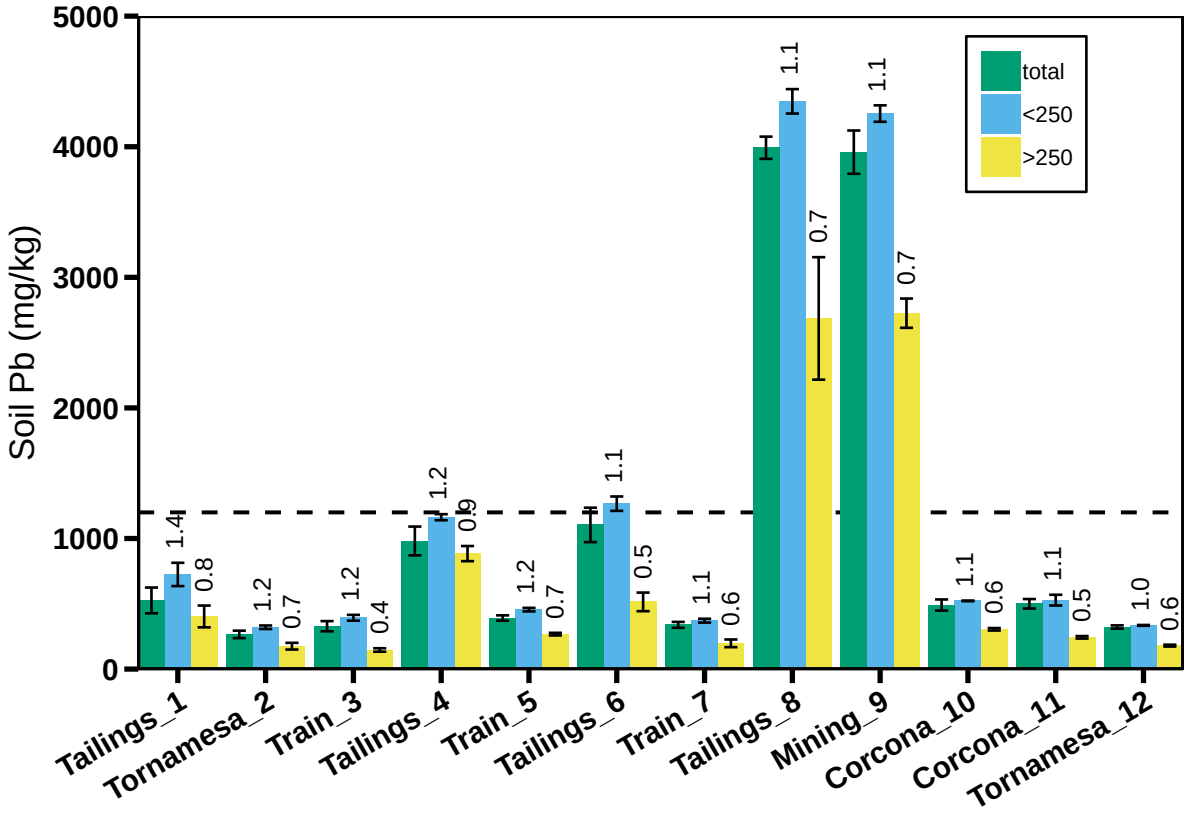

Figure B.9: Pb concentrations in the total soil sample, in the fine particle size (<250 μm), and large particle size (<250 μm). Samples are ordered in decreasing ratio of Pb (mg/kg) in the fine particle size to Pb in the total size fraction. Numbers on top of error bar indicate the ratio of Pb in the fine or large particle size to Pb in the total size fraction. Pb measured by XRF, and error bars are the standard deviation of three repeat measurements, shaking end-over-end between analyses in an attempt to capture heterogeneity. No clear difference seen between Corcona and Tornamesa or soil samples from the neighborhood built on mine tailings (tailings) in Corcona and the homes near the train tracks (train) in Tornamesa.

Appendix C

Supporting Information for Chapter 3

Hazardous levels of lead in soil identified with a kit by students in high school science classes

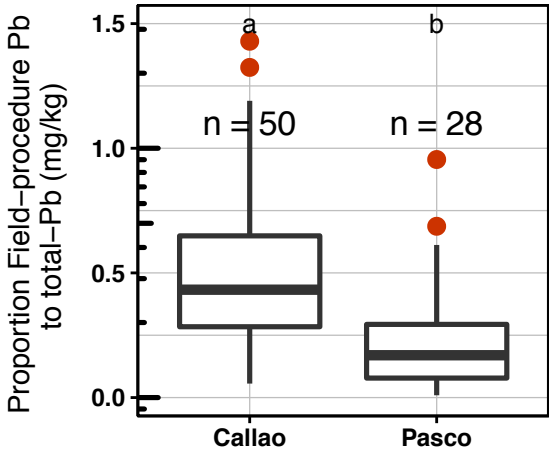

Figure C.1: Boxplot of proportion of field-procedure extractable Pb to total soil-Pb in Callao and Cerro de Pasco for samples with a pH of 3 or below. Outliers that extracted more than 100% Pb are, in part, because of inaccuracies of the XRF to measure low Pb concentrations ($<$ 10 mg/kg Pb) which are exacerbated when liquid Pb concentrations are multiplied by 10 to account for the 1.5 g in 15 mL solution.

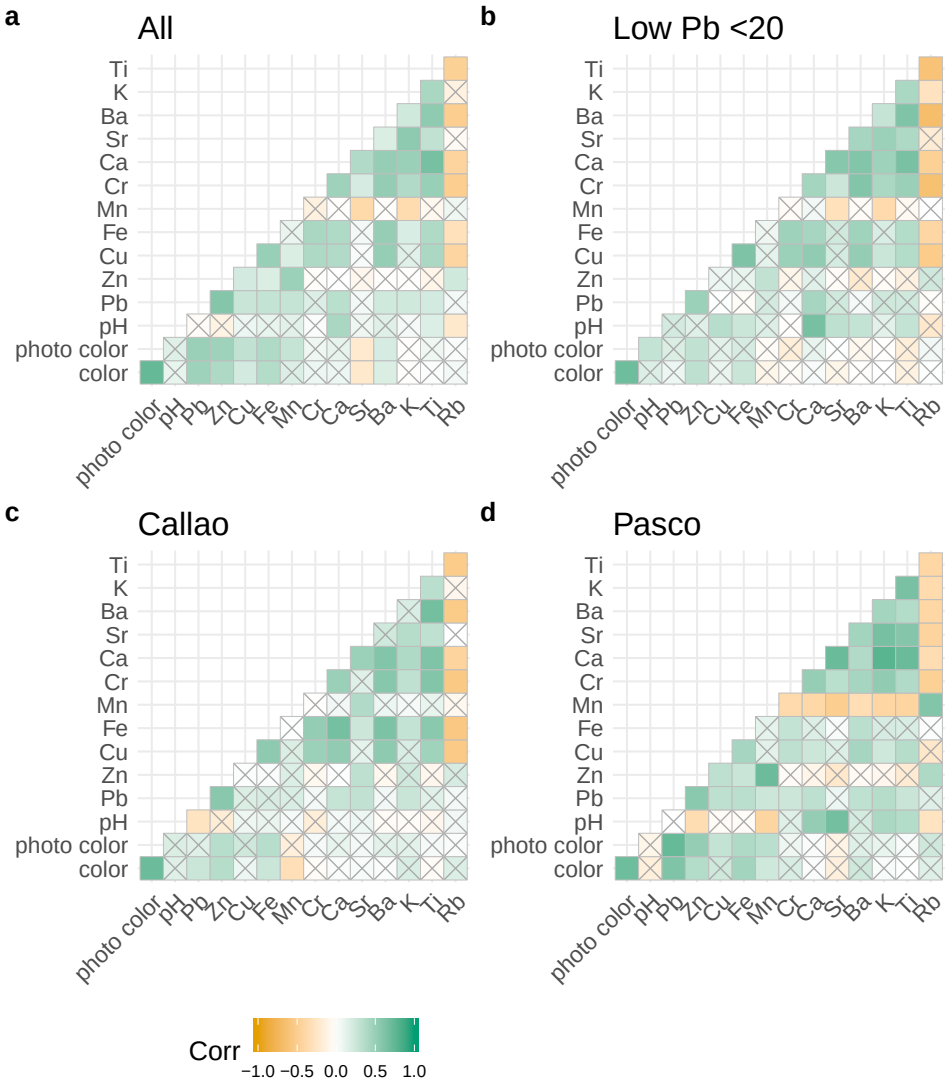

Figure C.2: Correlation of color result by elements in (a) all extract solution, as measured by XRF. Since Pb concentrations were significantly correlated with several other metals across all samples, only samples with less than 200 mg/kg Pb in the extract solution, before accounting for dilution, are shown to assess for possible interferences in low-Pb solutions. To compare contaminant sources, samples are separated by (c) Callao and (d) Cerro de Pasco. Only samples with a pH of 3 or lower are shown.

Appendix D

Supporting Information for Chapter 4

Elevated lead (Pb) concentrations and inventories in urban New York City

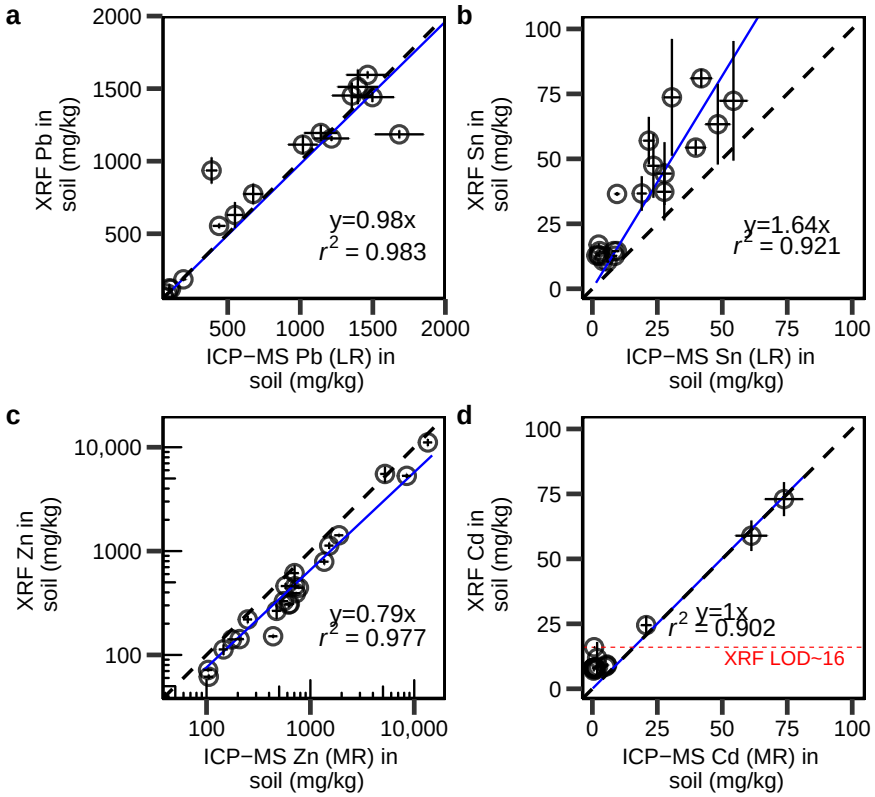

Figure D.1: Comparison of elemental concentrations analyzed by ICP-MS after full acid digestion of 0.2 g soil sample with concentrations measured by XRF on the hand-ground <1 mm core fraction. Best-fit line forced through the origin.

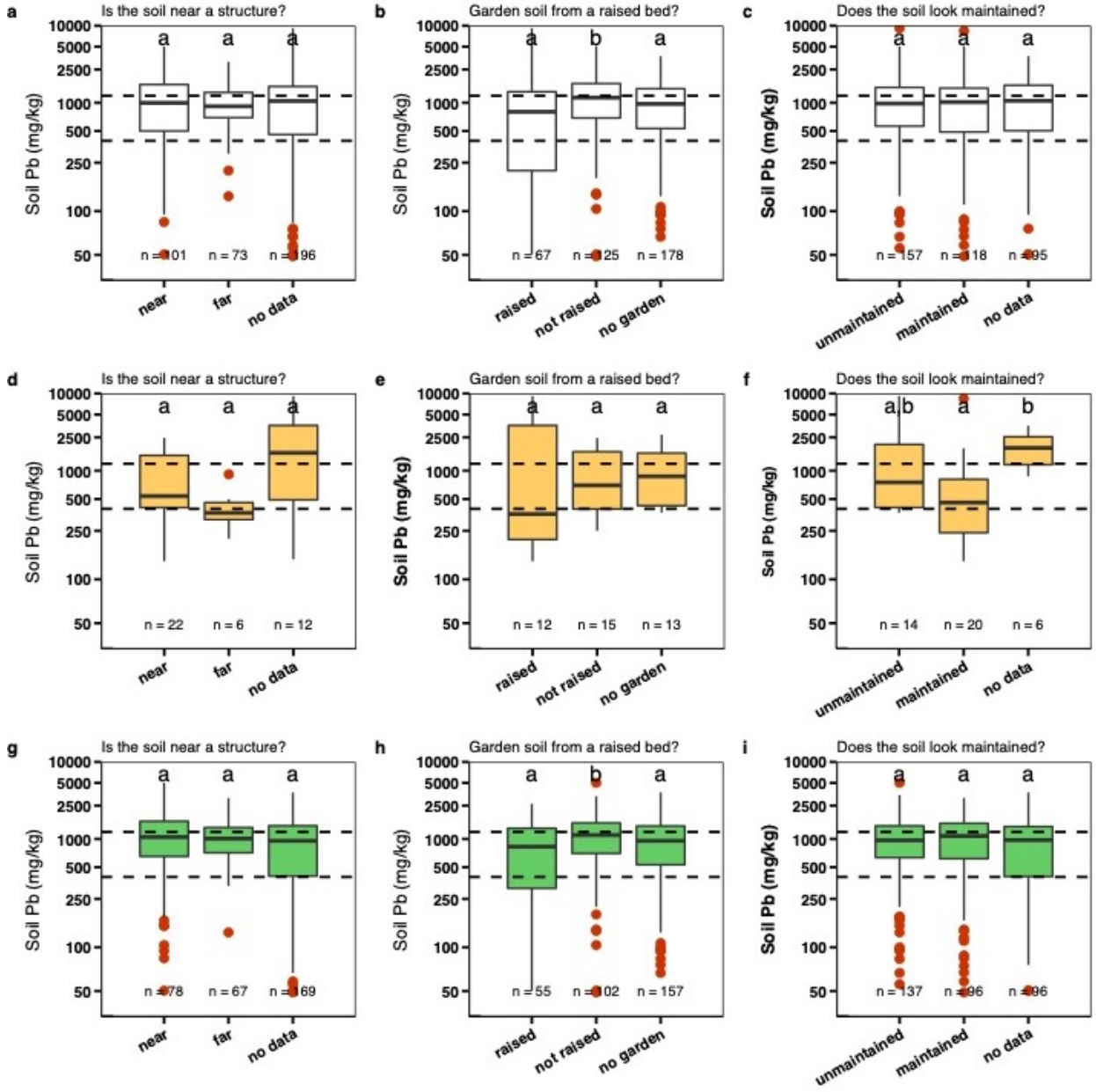

Figure D.2: Comparison of surface soil samples by sample description for samples from (top) all homes, (middle) Upper West Side homes, and (bottom) Greenpoint homes. Different letters indicate groups that are statistically different. Samples from Harlem are not included because of the small sample size (n=40), several categories with n=1 or 0).

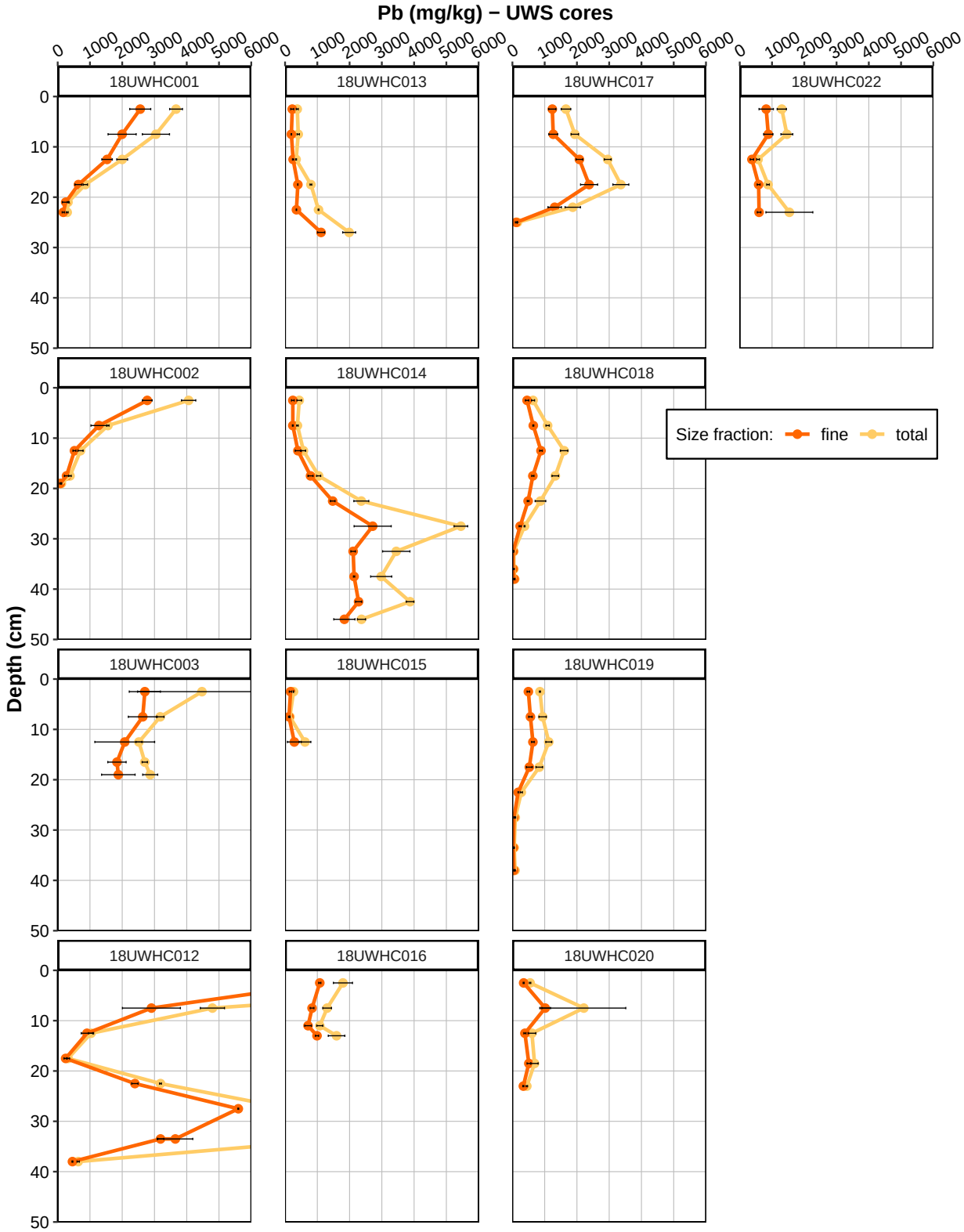

Figure D.3: Depth profiles of Pb concentrations in soil cores from the Upper West Side (UWS).

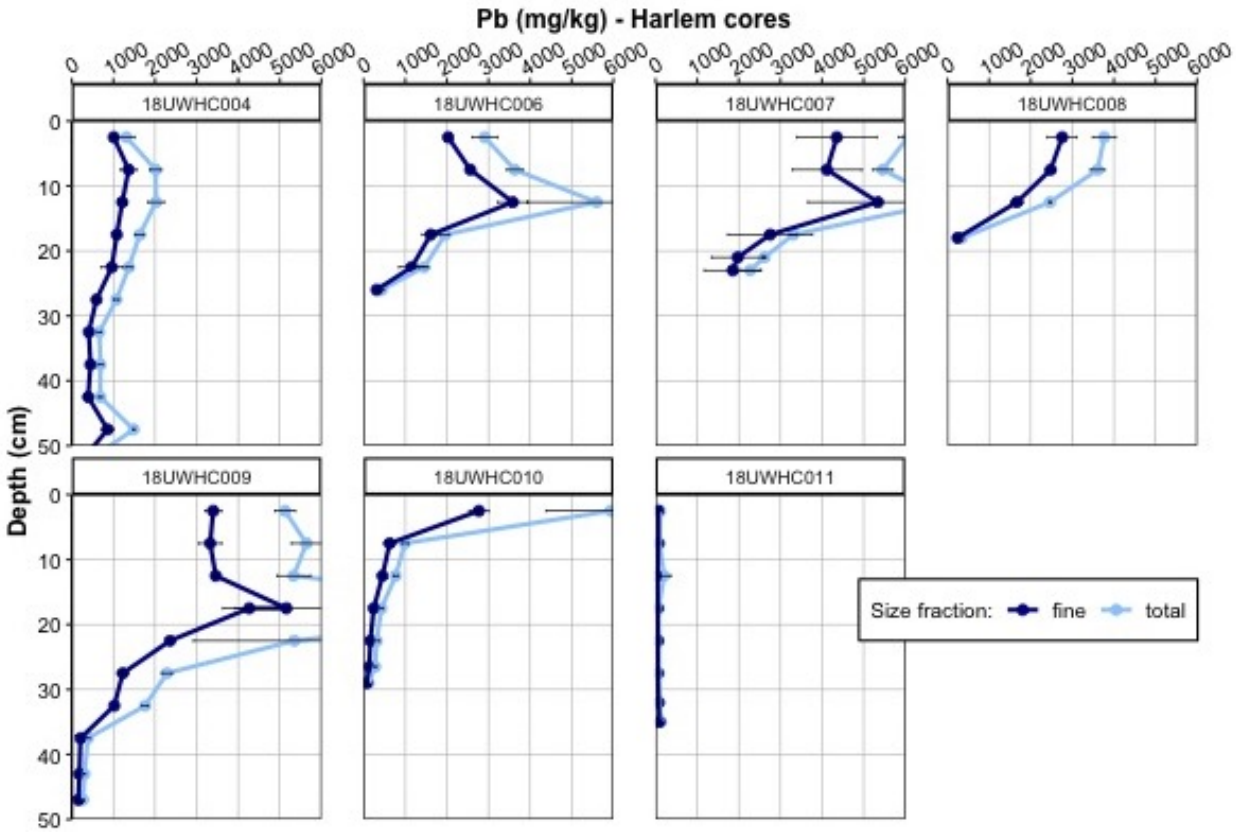

Figure D.4: Depth profiles of Pb concentrations in soil cores from Harlem.

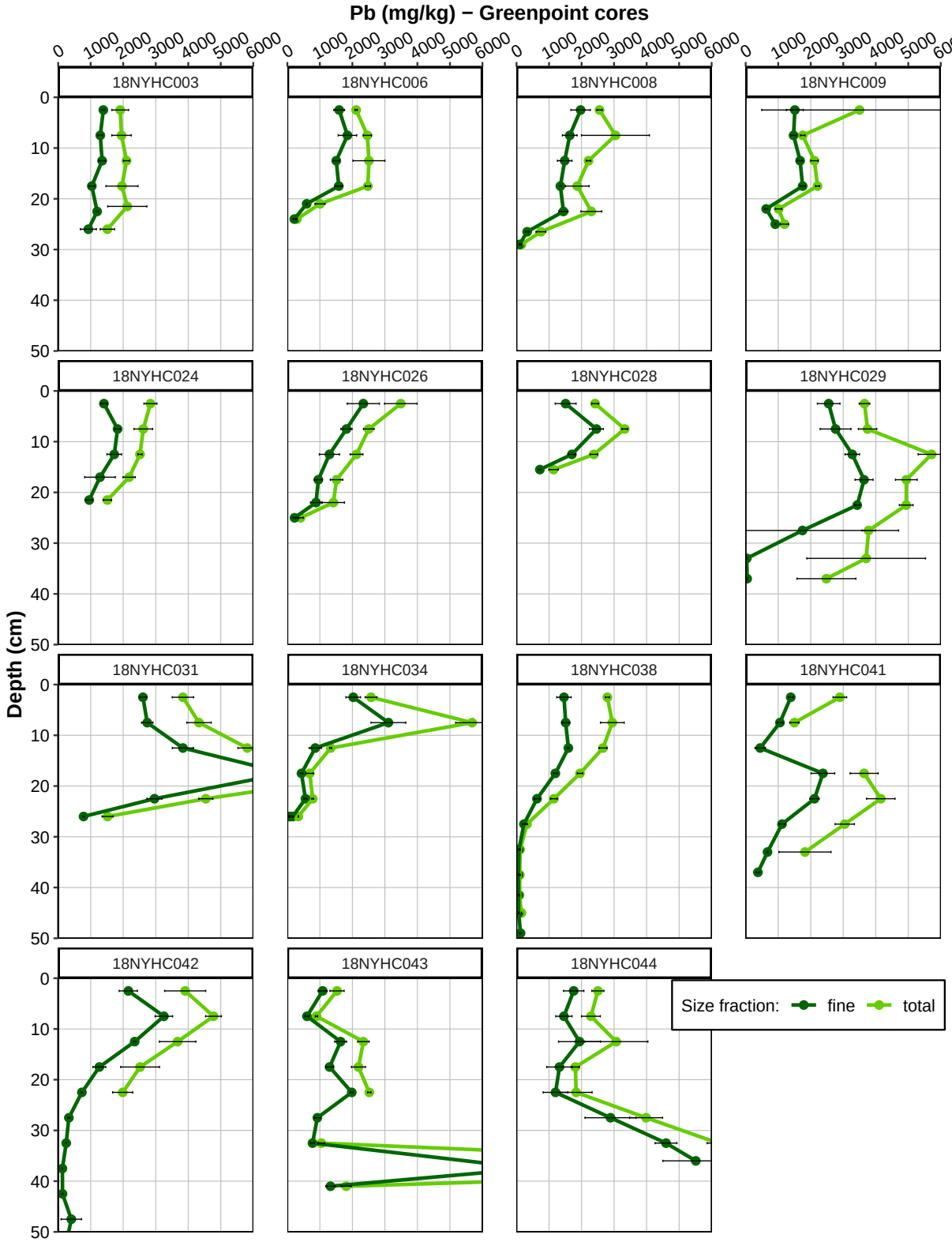

Figure D.5: Depth profiles of Pb concentrations in soil cores from Greenpoint.

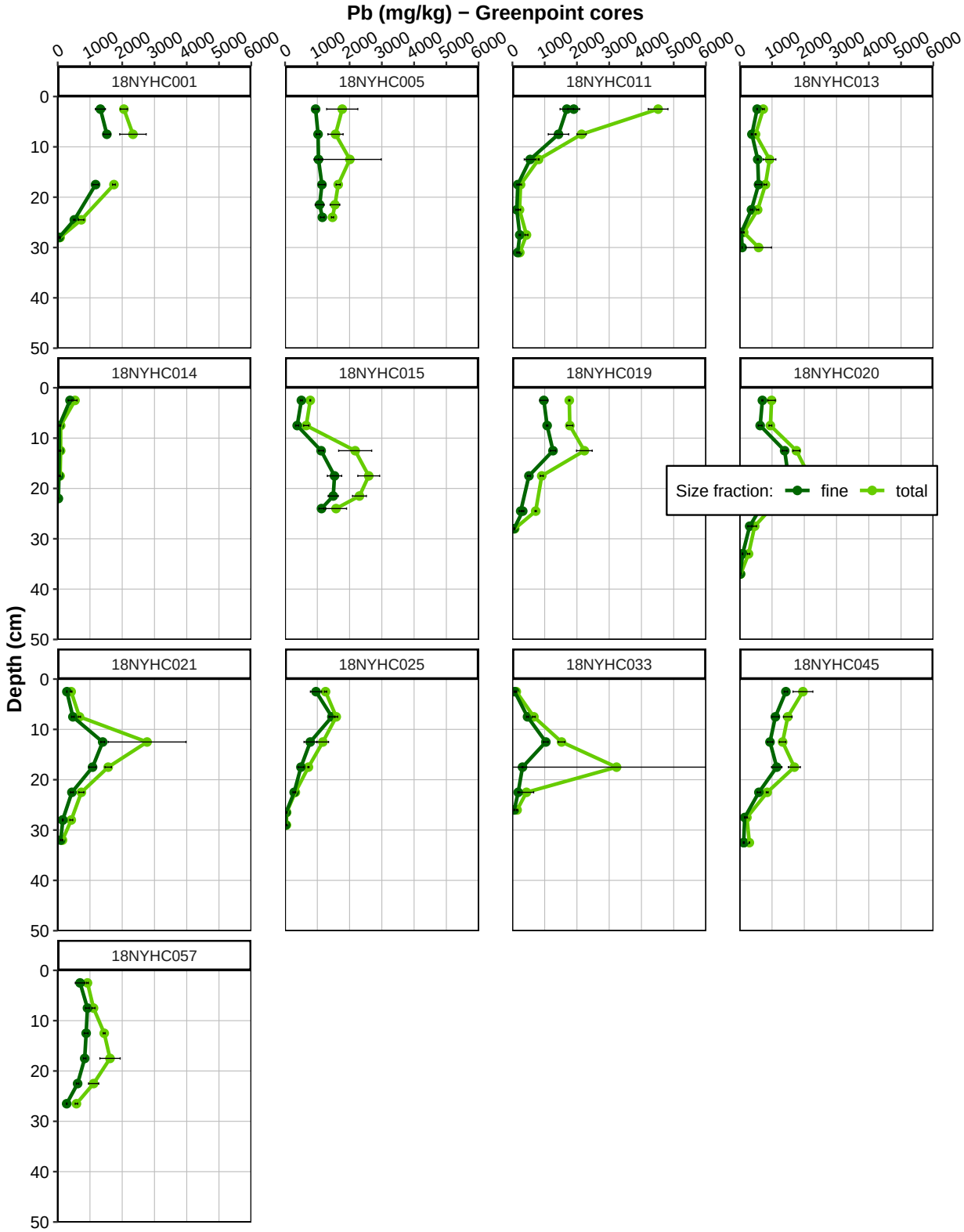

Figure D.6: Depth profiles of Pb concentrations in soil cores from Greenpoint.

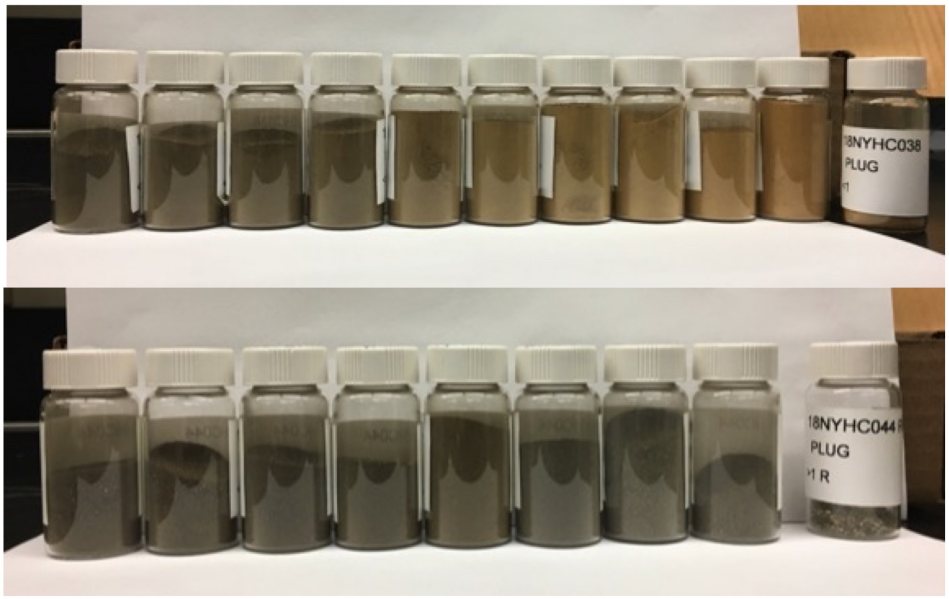

Figure D.7: (Top) Vials with 5 cm processed soil core intervals with typical colors from top (left) to bottom (right) going to background Pb concentrations (18NYHC038). (Bottom) Vials with unexpected colors of gray ash-like material and Pb concentrations increasing dramatically at depth (18NYHC044).